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New trends in chemistry teaching

Tendances nouvelles de l'enseignement de la chimie

Volume I

(1964-1965)

INSTITUTE OF EDUCATION
BANIPUR

The teaching of basic sciences
L'enseignement des sciences fondamentales

Chemistry
Chimie

Unesco

The teaching of basic sciences
L'enseignement des sciences fondamentales

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Tendances nouvelles de l'enseignement de la chimie

Vol. I

(1964-1965)

Edited for Unesco/Préparé pour l'Unesco
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Preface

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Unesco faces a heavy responsibility in helping the developing countries to improve their science teaching. These countries are aware that development depends upon the ability to train large numbers of their own people as scientists, engineers and technicians. They know, too, that they must bring about a widespread understanding of science among the entire population if they are to form a sound base for a modern technological society. Yet the very instruments with which they must carry out these tasks—their schools, technical institutes and universities—are weakened by obsolete practices and are overloaded by the vast increases in population and rapid growth in scientific knowledge.

Understandably, many of these countries have placed the highest priority upon a thorough modernization of their science education. In this work, they are searching for answers to a number of questions of central significance to the reorganization of science education along contemporary, rational and functional lines: Who should be taught? What should be taught? When should it be taught? How should it be taught? What balance should be kept between purely theoretical training and strictly practical apprenticeship? How much oral instruction from the teacher and how much individual study by the student is required? What is the role of the small group discussion, the class-room demonstration, the individual laboratory experiment, audio-visual aids including television in science education? In view of the need for scientific literacy among the entire population as a base for a technological society, what form of general science teaching can best bring about this widespread understanding of science?

Motivated by the search for answers to such questions, Unesco has developed a programme in science teaching whose main objectives are the following: (a) to promote the exchange of information on the content and methodology of science teaching; (b) to conduct experimental projects for developing new science-teaching methods and materials; (c) to organize, in collaboration with Member States, international post-graduate training programmes and to co-operate with Member States in the establishment of advanced training centres for scientists, teachers and research workers in developing countries; and (d) to stimulate interest in science and science teaching and to promote understanding of the impact of science in human affairs, by sponsoring lectures by distinguished scientists, and by making international awards such as the Kalinga Prize.

In publishing every two years within the collection "The Teaching of Basic Sciences", a series of volumes on new trends in this field, Unesco aims to provide an exchange of information on modern content, approaches, curricula and techniques in the teaching of the basic sciences. Each biennial series will consist of four volumes entitled *New Trends in . . .*, one on each of the three sciences, physics, chemistry and biology, and one on mathematics.

This first volume, *New Trends in Chemistry Teaching* has been drawn up in close collaboration with the Committee on the Teaching of Chemistry of the International Union of Pure and Applied Chemistry. On the recommendation of this committee, Mr. E. Cartmell of Southampton University (United Kingdom) was appointed as editor. In compiling the "New Trends" he has had the benefit of consultation with an editorial board consisting of: Professor P. Cadiot (France), Professor J. Arthur Campbell (United States), Dr. D. Chisman (United Kingdom), Dr. F. W. Gibbs (United Kingdom), Professor M. Oki (Japan) and Professor J. Zyka (Czechoslovakia).

Together with this editorial board the editor has collected papers published in 1964 in the leading science-teaching journals of the world and organized them into groups dealing with new developments in the class-room presentation of chemistry, new topics for inclusion in a modern syllabus of school or college chemistry, new laboratory and demonstration experiments, and reports on curriculum reform and new approaches to chemistry teaching in countries all over the world. Unesco gratefully acknowledges the readiness with which editors and publishers of journals have given permission for the reproduction of articles. The articles in this first volume have come from a limited number of journals, principally those appearing in English or French. Special arrangements regarding selection of articles and their translation into English and French have recently been worked out between Unesco and nations where chemical education journals are not published in English or French, e.g., U.S.S.R., Japan and the Scandinavian countries. As more of these special arrangements are concluded, future issues of "New Trends" will carry more contributions to chemistry teaching from these countries, ensuring a truly international character to "New Trends".

This first volume of *New Trends in Chemistry Teaching* is, in fact, an experiment—a first approximation to a useful means for placing vital information on chemistry teaching into the hands of as many science educators in the developing countries as possible at minimum cost and delay. The technical execution of the volume reflects this in its unconventional and non-uniform appearance which the editors hope the reader finds not too distracting.

This volume is intended to be used by chemistry teachers in universities, teacher-training institutions and secondary schools as well as university students of chemistry, especially those who are training to be teachers. But such additional groups of science educators as national science teachers' associations, science education sections of a Ministry of Education, and members of examination councils are likely to find information of real interest in this volume.

TO WHAT USE MIGHT THIS VOLUME BE PUT?

The contents have been selected to present a picture of areas in which chemistry is developing rapidly as well as to describe new teaching methods and approaches. Hence it should find use as a source book of such information for teachers-in-training and their tutors. It may also be used as a source of ideas for the development of new chemistry-teaching techniques and curricula. This collection should prove helpful to science teachers at all levels who must present new scientific knowledge in a manner students find comprehensible. It is suggested that "New Trends" be used as a basis for conducting seminars on the teaching of chemistry and for refresher courses for chemistry teachers.

Avant-propos

INSTITUTE OF EDUCATION

L'Unesco a la lourde responsabilité d'aider les pays en voie de développement à améliorer leur enseignement des sciences. Ces pays savent que tout progrès dans ce domaine est fonction de la possibilité qu'ils auront de former d'importants contingents d'hommes de science, d'ingénieurs et de techniciens. Ils savent aussi qu'il leur faut ouvrir toute la population à la science, pour établir les fondements solides d'une société technologique moderne. Or, les outils mêmes avec lesquels il leur faut mener à bien cette tâche — leurs écoles, instituts techniques et universités — n'ont pas l'efficacité voulue en raison des méthodes désuètes employées, et ils sont d'ailleurs dépassés par les événements : la forte poussée démographique et l'accroissement rapide des connaissances scientifiques.

Aussi nombre de ces pays ont-ils accordé la priorité absolue à la modernisation de leur enseignement scientifique. Ce faisant, ils sont en quête de réponses à un certain nombre de questions d'importance vitale pour la réorganisation de l'enseignement des sciences selon des critères modernes, rationnels et fonctionnels: Qui faut-il instruire? Que faut-il enseigner? Quand faut-il l'enseigner? Comment faut-il l'enseigner? Quel équilibre faut-il maintenir entre la formation purement théorique et l'apprentissage strictement pratique? Quelle doit être la part de l'enseignement magistral et quelle doit être celle des études individuelles? Quel doit être le rôle, dans l'enseignement des sciences, de la discussion en petits groupes, des applications pratiques en classe, du travail de laboratoire individuel, des auxiliaires audio-visuels y compris de la télévision? Étant donné la nécessité de donner un certain niveau de culture scientifique à la population tout entière, pour asseoir la société technologique de demain, quelle est la forme d'enseignement scientifique général qui donnera à cet égard les meilleurs résultats?

Cherchant à trouver réponse à toutes ces questions, l'Unesco a élaboré un programme d'enseignement des sciences dont les objectifs principaux sont les suivants: *a*) Favoriser les échanges de renseignements sur le contenu et la méthodologie de l'enseignement des sciences; *b*) Réaliser des projets expérimentaux en vue de la mise au point de méthodes et de matériels nouveaux pour l'enseignement des sciences; *c*) Organiser, en collaboration avec les États membres, des programmes internationaux d'études universitaires supérieures et coopérer avec les États membres à l'établissement de centres de hautes études à l'intention des hommes de science, des enseignants et des chercheurs des pays en voie de développement; *d*) Stimuler l'intérêt porté à la science et à l'enseignement des sciences, et faire mieux comprendre l'influence que la science exerce sur les affaires humaines en patronnant des tournées de conférences faites par des savants éminents et en décernant des prix internationaux comme le Prix Kalinga.

En entreprenant de publier tous les deux ans, au sein de la collection « L'enseignement des sciences fondamentales », des séries de volumes consacrés aux nouvelles tendances de cet enseignement, l'Unesco cherche à fournir l'occasion d'un échange d'informations sur le contenu, la conception générale, les programmes et les techniques modernes de l'enseignement des sciences fondamentales.

Chaque série biennale comprendra quatre volumes intitulés *Tendances nouvelles de ...* et dont trois seront consacrés chacun à l'une des sciences suivantes: physique, chimie, biologie, et le quatrième aux mathématiques.

Ce premier volume, *Tendances nouvelles de l'enseignement de la chimie*, a été établi en étroite collaboration avec le Comité de l'enseignement de la chimie, de l'Union internationale de chimie pure et appliquée. Sur la recommandation de ce comité, M. E. Cartmell, de l'Université de Southampton (Royaume-Uni), a été nommé rédacteur en chef. Il a bénéficié du concours d'un comité de rédaction composé des spécialistes suivants: professeur P. Cadiot (France), professeur J. Arthur Campbell (États-Unis), docteur D. Chisman (Royaume-Uni), docteur F. W. Gibbs (Royaume-Uni), professeur M. Oki (Japon) et professeur J. Zyka (Tchécoslovaquie).

En coopération avec ce comité, M. Cartmell a réuni des textes publiés en 1964 dans les principales revues mondiales d'enseignement des sciences et les a classés sous plusieurs rubriques : présentation moderne de la chimie en classe : nouveaux sujets à inclure dans un programme moderne d'étude de la chimie à l'école ou en faculté; nouvelles expériences et manipulations de laboratoire; réforme des programmes et nouvelles conceptions de l'enseignement de la chimie dans le monde. L'Unesco est heureuse d'exprimer sa reconnaissance aux directeurs et éditeurs de revue qui ont bien voulu autoriser la reproduction de leurs textes. Les articles de ce premier volume sont tirés d'un nombre limité de revues, surtout de langue anglaise ou française. Des dispositions particulières relatives au choix d'articles sur la chimie et à leur traduction en anglais et en français ont été récemment arrêtées entre l'Unesco et les pays qui ne sont ni anglophones ni francophones, comme l'URSS, le Japon et les pays scandinaves. Au fur et à mesure que de nouvelles dispositions de ce genre seront arrêtées, les tomes suivants de cet ouvrage comprendront de plus nombreux articles provenant de ces pays et portant sur l'enseignement de la chimie, ce qui assurera à la collection un caractère vraiment international.

Le présent volume est en fait une expérience, la première approximation d'un moyen pratique de fournir des renseignements essentiels sur l'enseignement de la chimie au plus grand nombre possible de professeurs de sciences des pays en voie de développement, à un prix et dans des délais minimaux. D'où la présentation technique du volume, son aspect inhabituel et son manque d'uniformité qui, espérons-le, ne distrairont pas trop l'attention du lecteur.

Ce volume est destiné aux professeurs de chimie exerçant dans les universités, les écoles normales et les établissements secondaires, aussi bien qu'aux étudiants en chimie, surtout s'ils se destinent au professorat. Mais d'autres collectivités enseignantes telles que les associations nationales de professeurs de sciences, les services d'enseignement des sciences de ministères de l'éducation et les membres des jurys d'examen y trouveront sans doute des renseignements d'un réel intérêt.

A QUELLES FINS UTILISER CE VOLUME?

Le contenu en a été choisi de façon à présenter une fresque des domaines où la chimie progresse à pas rapides, et à décrire les conceptions et méthodes nouvelles d'enseignement. Il devrait donc constituer, dans ce domaine, une source utile de renseignements pour les étudiants qui se destinent à l'enseignement et pour leurs professeurs. On peut aussi y puiser des idées pour la mise au point de techniques et de programmes nouveaux pour l'enseignement de la chimie. Cet ouvrage devrait être utile aux professeurs de sciences à tous les niveaux, puisqu'ils doivent présenter les connaissances scientifiques nouvelles d'une façon qui soit accessible aux étudiants. On peut enfin le proposer comme document de base pour des stages d'études sur l'enseignement de la chimie et pour les cours de recyclage de professeurs de chimie.

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Foreword

It gives me much pleasure to welcome, on behalf of our Committee, this first volume produced by Unesco dealing with *New Trends in Chemistry Teaching*. The organizers have been fortunate in being able to secure the services of Mr. Edward Cartmell as editor, as is evidenced by the excellent choice of articles for this first issue. The Committee on the Teaching of Chemistry of the International Union of Pure and Applied Chemistry (IUPAC) has, as one of its main aims, the provision of advice on modern methods of chemistry teaching and it was therefore very happy to collaborate with Unesco in advising on the choice of an editor and in commenting on the nature of the proposed annual review and the contents therein.

The teaching of science has been criticized ever since science has been taught but during the past few years this criticism has become world-wide and more purposeful in its objective. The rapidly increasing mass of factual material which is available to the teacher of chemistry has focused attention on the need for careful selection of the material to be taught and on the need for a careful defining of the objectives of teaching chemistry in a modern world. Clearly emerging from all of the experimental teaching programmes in various countries is the conviction that chemistry should be taught so as to develop genuine understanding by the pupil, to encourage him to inquire for himself and to develop capacity for judgement. Chemistry is, of course, concerned with the behaviour of substances, and the acquisition of a body of fact, obtained by the student as far as possible by his own investigations and discovery, is absolutely essential. The big challenge to teachers is to find the right balance between facts, principles and methods of approach by students at various levels of development.

One way in which we can develop our ideas is for us to compare and contrast the approaches adopted in various countries by colleagues interested in similar problems. This collection of excellent articles should do much to assist this healthy exchange of modern views for the mutual benefit of us all.

R. S. Nyholm, F.R.S.
Chairman, Committee on the Teaching of Chemistry
of the International Union of Pure and Applied
Chemistry.

Section 1 Atomic structure and the periodic table

The article by the Chairman of the IUPAC Commission on Atomic Weights, clearly sets out the reasons which have led to the adoption of the carbon-12 scale, and contains a table of atomic weights which readers may find convenient. Curriculum reform usually begins by introducing modern ideas on atomic structure. This is now dealt with in a large number of textbooks at all levels. A short account will be found in Chapter 4 of *Chemistry To-day: a Guide for Teachers*, OECD, Paris. The intelligent student will see diagrams of *s*, *p* and *a* orbitals in many textbooks, but he will rarely find a description or diagrams of *f* orbitals, although he will hear about these in any comprehensive discussion of the periodic table. The papers on *f* orbitals reproduced here will give the teacher some material with which to answer queries which frequently arise. The articles also explain the significance of subscripts (such as *xy* in *axy*) used to designate particular *a* (or *f*) orbitals. (See also the article by Cotton on page 90 for descriptions of *a* orbitals.) Articles on the periodic table are legion. I have selected one by E. Pachmann *et al.*, which gives some useful hints on designing colour codes to highlight the changes in particular properties, such as electronegativity, with the position of an element in the table. A very helpful article by B. Englund of Uppsala, Sweden, on an experimental approach to the periodic system will be found in Chapter 3 of the OECD publication, *Chemistry To-day*.

Reprinted from Chemistry, Vol. 37, No. 3, 1964, pp. 12-17.

Why the Carbon-12 Scale?

In 1961 a new table of atomic weights was adopted. The atomic weight of oxygen, for long assigned the exact value of 16, was changed to 15.9994. In the new table no element is assigned an integral atomic weight. The story of atomic weight scales and the reasons for the most recent change are outlined by the chairman of the Commission on Atomic Weights of the International Union of Pure and Applied Chemistry.

When the atomic theory of the constitution of matter gained general acceptance, early in the 19th century, one of the important conclusions drawn from it was that the masses of all atomic particles of a given chemical element are identical and that they differ from the atomic masses of all other elements. This concept was the keystone in the structure of chemistry, then in its beginnings as a quantitative science, and remained unchallenged until the existence of isotopes was discovered, a hundred years later.

Let us for the moment imagine ourselves to be back in the early 19th century, secure in the belief that the atomic masses of the elements are constants of nature. We would be concerned with two related problems. One would be to learn the magnitude of the mass of a single atomic particle as a physical quantity. This problem was not to be solved until after the close of the century, a fact that is not surprising when we realize that an atom of oxygen has a mass of slightly less than 3×10^{-23} gram.

An alternative would be to determine the masses of atoms of different elements relative to one another. The solution to this problem was within reach. It was necessary only to draw certain logical conclusions from two kinds of observations about the proportions in which chemical elements react to form compounds. One type of observation showed that the reaction of two substances to form another substance always involved the same proportions by weight of the reactants and of the product. The other disclosed that reactions between gaseous substances always involved simple numerical ratios between the volumes of the reactants and of the product, if also gaseous. A necessary proviso was that all volumes were measured at the same pressure and at the same temperature. The latter kind of observations led to Avogadro's hypothesis that equal volumes of gases of any kind at the same pressure and temperature contain equal numbers of molecules. If now one determined the relative densities of the gaseous reactants and product—that is, their weights per unit volume—the relative weights of the molecules could be readily calculated. When further observations led to increasingly firm conclusions about the number of atoms that composed the molecules of gases, the known relative weights of the reacting molecules were easily converted to relative atomic masses.

By analogous reasoning it followed that nongaseous substances also could be expected to combine in simple numerical ratios of atoms and that the relative masses of the reacting atoms could be deduced from the observed ratios of combining weights. Thus, if it was observed that copper reacted with oxygen to form two different compounds, the weight of oxygen involved in the reactions for a given weight of copper would be found to be exactly twice as great for one compound as for the other. From this it was clear that an element could have more than one combining weight with another element but, in that case, there would be a simple numerical relationship between the combining weights. When this was confirmed by similar experiments with other elements, such as iron or lead, trial assignments of molecular formulas could be made. In the case of copper the simplest and most plausible formulas would be CuO and Cu_2O. On this basis the relative atomic mass of copper, referred to that of oxygen, would be identical with the smaller of the two combining weights of copper with oxygen. If we measured the combining weights with oxygen of a group of elements—for example, hydrogen, copper, iron, and selenium—and we knew from certain other observations that the numbers of atoms in the four oxides had the following ratios: $\frac{2H}{O}$, $\frac{Cu}{O}$, $\frac{2Fe}{3O}$, and $\frac{Se}{2O}$, we would need only to take some arbitrary number as the atomic mass of the element (oxygen) which is common to all the ratios in order to place the atomic masses of the other elements on a common scale. The assigned atomic mass of oxygen would be the denominator of that scale.

(Continued on page 15)

TABLE OF RELATIVE ATOMIC WEIGHTS 1961

Based on the Atomic Mass of $C^{12} = 12$

The values for atomic weights given in the table apply to elements as they exist in nature, without artificial alteration of their isotopic composition, and further, to natural mixtures that do not include isotopes of radiogenic origin.

Name	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	. . .
Aluminum	Al	13	26.9815
Americium	Am	95	. . .
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	. . .
Barium	Ba	56	137.34
Berkelium	Bk	97	. . .
Beryllium	Be	4	9.0122
Bismuth	Bi	83	208.980
Boron	B	5	10.811[a]
Bromine	Br	35	79.909[b]
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	. . .
Carbon	C	6	12.01115[a]
Cerium	Ce	58	140.12
Cesium	Cs	55	132.905
Chlorine	Cl	17	35.453[b]
Chromium	Cr	24	51.996[b]
Cobalt	Co	27	58.9332
Copper	Cu	29	63.54
Curium	Cm	96	. . .
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	. . .
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	. . .
Fluorine	F	9	18.9984
Francium	Fr	87	. . .
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.967
Hafnium	Hf	72	178.49
Helium	He	2	4.0026
Holmium	Ho	67	164.930
Hydrogen	H	1	1.00797[a]
Indium	In	49	114.82
Iodine	I	53	126.9044
Iridium	Ir	77	192.2
Iron	Fe	26	55.847[b]
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.9380
Mendelevium	Md	101	. . .
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.183
Neptunium	Np	93	. . .
Nickel	Ni	28	58.71
Niobium	Nb	41	92.906
Nitrogen	N	7	14.0067
Nobelium	No	102	. . .
Osmium	Os	76	190.2
Oxygen	O	8	15.9994[a]
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Plutonium	Pu	94	. . .
Polonium	Po	84	. . .
Potassium	K	19	39.102
Praseodymium	Pr	59	140.907
Promethium	Pm	61	. . .
Protactinium	Pa	91	. . .
Radium	Ra	88	. . .
Radon	Rn	86	. . .
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.905
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.35
Scandium	Sc	21	44.956
Selenium	Se	34	78.96
Silicon	Si	14	28.086[a]
Silver	Ag	47	107.870[b]
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulfur	S	16	32.064[a]
Tantalum	Ta	73	180.948
Technetium	Tc	43	. . .
Tellurium	Te	52	127.60
Terbium	Tb	65	158.924
Thallium	Tl	81	204.37
Thorium	Th	90	232.038
Thulium	Tm	69	168.934
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03
Vanadium	V	23	50.942
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.905
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

[a] Atomic weights so designated are known to be variable because of natural variations in isotopic composition. The observed ranges are:

Boron	±0.003
Carbon	±0.00005
Hydrogen	±0.00001
Oxygen	±0.0001
Silicon	±0.001
Sulfur	±0.003

[b] Atomic weights so designated are believed to have the following experimental uncertainties:

Chlorine	±0.001
Chromium	±0.001
Iron	±0.003
Bromine	±0.002
Silver	±0.003

Since we are dealing only with relative atomic masses, it does not matter what number is arbitrarily assigned as the denominator. Berzelius, one of the early and great systematizers of the new quantitative chemistry, assigned 100 as the relative atomic mass of oxygen and used this number as the denominator by which all other atomic masses were defined. Others, observing that hydrogen had the smallest relative atomic mass, considered it logical to give an assigned atomic mass of unity to that element. The hypothesis of Prout (1815) that the atom of hydrogen was the structural unit of the atoms of all the elements gave support to this idea. On this basis all atomic masses should be whole numbers. As we know, the atomic masses of a number of common elements approximate whole numbers, if referred to that of hydrogen as unity. Of course many others do not, and a long time passed before the reason for this apparent discrepancy was understood.

The fact that combining weights of elements with oxygen were more easily measured than those with hydrogen caused a return to the Berzelius idea of using oxygen as the reference element for a scale of atomic masses, but with an assigned value of 16 instead of 100. This kept the atomic mass of hydrogen at approximately 1 (actually 1.008) but got around the experimental difficulties of measurements that involved hydrogen. For some years in the early 1900's it was common practice to publish the results of atomic mass determinations on both bases. Text and reference books of that period commonly contained two "Tables of Atomic Weights," one headed H=1 and the other headed O=16. Gradually the hydrogen-based scale fell into disuse.

Indirect Atomic Mass Comparisons

It should be clear from what has been said that it was not necessary to determine atomic masses by direct comparison with oxygen. Other combining weight ratios would answer provided the atomic masses of at least one of the elements involved had been accurately related to that of oxygen. In fact, much of the most accurate work on the measurement of atomic masses in the first quarter of the present century was done by measuring the weight of the chloride (or bromide) of an element that reacted quantitatively with a known weight of silver to form silver chloride (or bromide). A classical determination of this kind was used to derive the atomic mass of sodium from the exact weight of sodium chloride required to precipitate all of a known weight of silver from its solution in nitric acid. The ratio of the reacting weights of the two substances is equal to the ratio of the molecular mass of sodium chloride to the atomic mass (At. mass) of silver. The equation is

$$\frac{\text{Wt. of NaCl}}{\text{Wt. of Ag}} = \frac{\text{At. mass of Na} + \text{At. mass of Cl}}{\text{At. mass of Ag}} \tag{1}$$

This equation can be solved for the atomic mass of sodium only with the help of other equations that will give us values for the atomic masses of silver and chlorine. The value for the atomic mass of silver was obtained by determining the weight of silver nitrate that was formed from a known weight of silver by dissolving the metal in nitric acid, evaporating the solution to dryness and fusing the residue. The equation is

$$\frac{\text{Wt. of Ag}}{\text{Wt. of AgNO}_3} = \frac{\text{At. mass of Ag}}{\text{At. mass of Ag} + \text{At. mass of N} + 3 \times 16} \tag{2}$$

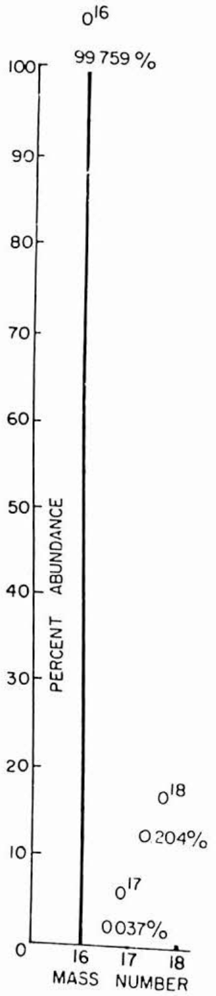
This equation required for its solution a value for the atomic mass of nitrogen which was obtained by another reaction which will not be described here. However, to go back to Equation 1, it is still necessary to find the atomic mass of chlorine. To get this, a known weight of silver was dissolved in nitric acid and the solution treated with hydrochloric acid. The silver chloride thus formed was collected and weighed. The equation is a simple one,

$$\frac{\text{Wt. of AgCl}}{\text{Wt. of Ag}} = \frac{\text{At. mass of Ag} + \text{At. mass of Cl}}{\text{At. mass of Ag}} \tag{3}$$

If this seems a laborious and roundabout way of determining the atomic mass of sodium on the O=16 scale, it should be remembered that once silver had been related to oxygen and chlorine to silver, the general procedure of comparing a chloride with silver proved extremely useful for determining many atomic masses. T. W. Richards received the Nobel Prize for chemistry in 1914 for his development and perfection of these procedures at Harvard University.

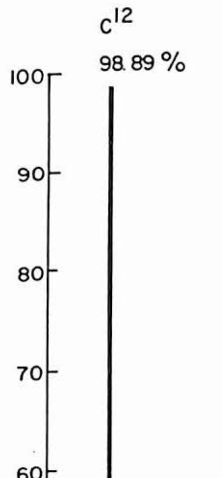
Elements Exist in Two or More Forms

We come now to the new problem introduced by the discovery that many elements, in fact most of them, exist in nature in two or



Per cent abundances of isotopes (by numbers of atoms) in naturally occurring oxygen

When the minute amounts of O^{17} and O^{18} were discovered, physicists used the mass of the O^{16} isotope as their standard of mass 16, while chemists assigned this value to the average isotopic mass of naturally occurring oxygen



Per cent abundances of isotopes in naturally occurring carbon
The new atomic weight scale assigns the whole number 12 to the carbon-12 isotope—that is, to the isotope whose nucleus contains six protons and six neutrons

more isotopic forms. For such an element, the supposed atomic mass was, in fact, the average atomic mass of its naturally occurring mixture of isotopic forms. The importance of knowing the "atomic mass" was not affected by this fact except in the relatively unusual situation in which isotopic differentiation occurred. For example, in assaying an iron ore it does not matter that the "atomic mass" used in the calculation is the average atomic mass of several isotopes, all of which behave chemically as iron. However, problems arose when mass spectroscopy came into use for measuring atomic masses. In this technique the isotopes are differentiated in the process of measurement. In the mass spectroscope, charged atoms (ions) moving at a given velocity in a magnetic field follow curved paths whose curvature is a function of the mass and charge of the particle. This property of the atoms has in recent years provided an extremely accurate means of measuring relative atomic masses. However, in its beginning the method was not sufficiently sensitive to reveal the existence of minor proportions of isotopes. For example, the existence of small amounts of the oxygen isotopes of mass numbers 17 and 18 escaped notice for several years after the mass spectroscope was invented. For this reason, when atomic masses were first measured by mass spectroscopy relative to oxygen, it was supposed that the oxygen whose mass was being compared was exactly the same as that used in a classical combining-weight determination. But when O^{17} and O^{18} were discovered, it was realized that atomic masses compared in the mass spectroscope with the atomic mass of oxygen were really comparisons with the mass of O^{16}. However, physicists continued to use the whole number 16 as the assigned relative mass of this special oxygen. In doing this they abandoned the denominator of the classical scale of atomic masses and established a new scale, which became known as the physical scale to distinguish it from the other, or chemical scale. Because natural oxygen contains only traces of O^{17} and O^{18} the two scales were very nearly alike. The ratio of the "atomic weight" of the element oxygen (average atomic mass of the three isotopes) to the atomic mass of O^{16} is about 1.00028:1.

The Search for a Single Scale

Thus there came into use once again two scales of atomic masses, just as there had been when atomic weights were based either on H=1 or on O=16. However, the difference between the two oxygen scales was much smaller—so much so that it became difficult to avoid confusion. In calculations involving such an important natural constant as Avogadro's number, it was always necessary to specify whether the number used was based on the chemical or on the physical scale. Sometimes the authors of scientific papers neglected to give this information, even when they were dealing with quantities that had been measured precisely enough to be affected by the difference between the two scales.

It was recognized that the problems arising from the use of two slightly different scales could be solved by abandoning one of them. However, physicists did not like to return to the chemical scale because it was known that the relative abundances of the three isotopes of oxygen were somewhat different in the major natural sources of oxygen—air, water, and rocks. Hence the relative atomic mass of the element oxygen was slightly variable. While this variability was too small to affect the usefulness of chemically derived atomic masses, it did affect the highly precise physical measurement of the atomic masses of individual nuclides. Furthermore, on the chemical scale the atomic mass of not a single nuclide would have been an exact whole number. The atomic mass of O^{16}, for instance, would be $\frac{16}{1.00028}$ or 15.9956.

For chemists it would have been relatively easy to change to the physical scale had it not been for the existence of an enormous number of published data based on the old scale. A million or more published numerical quantities important to physical chemistry were believed to be sufficiently accurate so that a significant error would be introduced into them if they were not converted systematically to the new basis. The task of revising all such numerical data in text and reference books and in the periodical literature seemed impossibly great.

Earlier it was said that *any* chemical element would serve as well as any other for the reference element in a scale of atomic weights, provided means were available for relating its atomic mass to that of one or more other elements. This ceased to be true when isotopes were discovered, and the possibility of variations in natural isotopic composition was realized. The choice of a reference *element* should be limited to those elements that have no naturally occurring isotopes, if the number assigned to its atomic mass is to be a true constant. There are 21 such elements. Of the 21, fluorine is the only one whose atomic mass on the old chemical scale was very nearly an integral number (19). The adoption of F=19 as the denominator of a new scale would not have introduced a large enough error into published data to necessitate their revision. Such a scale therefore might have been acceptable to chemists. However, it was not acceptable to physicists for a number of reasons, one of which is that fluorine is not a good operating standard for mass spectroscopy.

C^{12} Chosen Reference Nuclide

Actually the choice of a reference species need not be limited to elements. A nuclide can be used just as well, provided means are available for accurately relating its atomic mass to other atomic masses, including the average atomic masses of the mixtures of nuclides that exist in nature as elements. After discussion about a new scale to replace both the chemical and physical scales had gone on for several years, it was realized that the principal isotope of carbon, C^{12}, would serve very well as the reference nuclide. This isotope had been for some time the principal working standard for measuring atomic masses by mass spectroscopy. This was because carbon forms so many hydrocarbons from which ionized hydrocarbon fragments can be obtained that one or another of them could be used for comparisons throughout the entire range of atomic masses of the elements.

For example, the hydrocarbon 3,4-benzophenanthrene ($C_{18}H_{12}$), when bombarded with electrons in a mass spectrometer, breaks up into some 200 identifiable ionized fragments with relative masses ranging, almost in one-unit steps, all the way from that of H^+ to that of the ionized molecule itself, $C_{18}H_{12}^+$. Accurate atomic mass measurements in the mass spectrometer depend on comparing the mass of an "unknown" particle with that of a standard particle of very nearly the same mass. (This is a typical case of achieving accuracy in measurements by determining small differences.) Thus, ions of $V^{51}+$, the principal isotope of vanadium, can be compared with $C_4^{12}H_3^1+$, which has a mass of 51, and $Ru^{101}+$ with $C_8^{12}H_5^1+$, which has a mass of 101.

If C^{12} were now to become the primary standard, with an assigned relative mass of exactly 12, the extra experimental work of comparing C^{12} with O^{16} would no longer be necessary.

Fortunately the atomic mass of C^{12} on the old chemical scale differs from the whole number 12 by only about 4 parts in 100,000. This difference is smaller than the estimated uncertainty of any except a very few published physicochemical data. Hence a conversion from the chemical scale to a scale based on $C^{12} = 12$ would not involve the enormous task of revising the published data. This fact made the C^{12} scale acceptable to chemists. For physicists, changes in numbers required by the change in scale from $O^{16} = 16$ to $C^{12} = 12$ were ten times larger. However the number of published data (mainly the atomic masses of several hundred nuclides) was much smaller. The advantages of a unified scale were sufficiently clear so that the C^{12} scale was adopted by the International Union of Pure and Applied Physics in 1960 and by the International Union of Pure and Applied Chemistry in 1961. The new scale has already gained world-wide acceptance among working scientists in all disciplines.

In the International Table of Relative Atomic Weights (see page 14), as adopted in 1961, there were two kinds of changes from the official table (of 1957). One kind resulted from the change of scale. Such changes amounted to 0.004% (note the change for oxygen from the exact number 16 to 15.9994) and were too small to affect more than a few of the values in the table. Others resulted from a systematic review and recalculation of the experimental work that had been done on each of the elements. For a report on these recalculations, see *J. Am. Chem. Soc.* 84, 4175 (1962). Atomic weights do not appear in the table for any of the radioactive elements, either natural or synthetic, other than thorium and uranium. The reason for this is that the isotopic compositions of such elements, and consequently their atomic weights, vary with the sources from which they are obtained.

Be^{9} F^{19} Na^{23}
Al^{27} P^{31} Sc^{45}
Mn^{55} Co^{59} As^{75}
Y^{89} Nb^{93} Rh^{105}
I^{127} Cs^{133} Pr^{141}
Tb^{159} Ho^{165} Tm^{169}
Au^{197} Bi^{209} Th^{232}

Mononuclidic elements

DR. EDWARD WICHERS was born in Michigan in 1892 and completed his undergraduate education at Hope College in 1913. After receiving the Ph.D. degree at the University of Illinois in 1917, he became a member of the staff of the National Bureau of Standards. He served at the bureau until his retirement, as associate director, in 1962, except for the years 1944–45, which were devoted to research in uranium chemistry and special reagents at the Los Alamos laboratory. He is now executive secretary of the Division of Chemistry and Chemical Technology of the National Research Council.

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The Shapes of the *f* Orbitals

The shapes of the *s*, *p*, and *d* orbitals are familiar to all students of modern chemistry, while the shapes of the *f* orbitals are relatively unknown. Although the equations for the *f* orbitals are readily available, meaningful illustrations are difficult to find, either in research journals or in chemistry textbooks. A few advanced texts (e.g., that by Pauling and Wilson (*1*)) present plots of the θ part of the *f* wave functions. However, at best, these are only cross sections of the *f* orbitals, and are not necessarily good indications of the overall shapes. In this paper, we have attempted to present illustrations of the shapes of *f* orbitals which may be of interest to students of inorganic chemistry.

One reason for the neglect of the *f* orbitals is the generally accepted belief that they have little or no effect on bonding. Although the *f* orbitals certainly do not play as important a role in bonding as do the *d* orbitals, their involvement may account for some of the more subtle aspects of the chemistry of the elements with atomic number 51 to 70 and 83 to 102. Hugus in an interesting paper (*2*) several years ago suggested that the 4*f* orbitals may be involved in bonding to some extent in the elements a few atomic numbers lighter than lanthanum. The enhanced stability of the higher oxidation states of antimony, tellurium, and iodine relative to those of arsenic, selenium, and bromine, respectively, was attributed to the contribution of the 4*f* orbitals to the total bonding In addition, it has been suggested (*3*) that the 4*f* orbitals in the lanthanide elements may be split in complexes by ligand fields, resulting in as much as a 10% increase in complex stability in the most favorable cases. This latter suggestion has not yet definitely been verified by experiment although there is inconclusive evidence (*4*) to support it. The 5*f* orbitals of the actinide elements seem to be available for participation in bonding, at least up to plutonium. Thus, the stability of the MO_2^{++} and MO_2^+ ions (M = U, Np, or Pu) has been attributed (*5*) to participation of 5*f* orbitals in bond formation. A distinct difference in behavior toward ion exchange resins between the lanthanide ions and the transplutonium actinide ions in concentrated hydrochloric acid solution has been explained, also, by greater involvement of the 5*f* orbitals in bonding (*6*).

The *f* orbital pictures in this paper are based on the angular part of the hydrogenic wave functions. These are found, for example, in Appendix III of the third edition of *The Nature of the Chemical Bond* (*7*), and in a paper by J. C. Eisenstein (*8*). (Pauling and Eisenstein used different normalizing factors, resulting in equations that differ by the factor $\sqrt{4\pi}$.) The orbitals are usually represented in a spherical coordinate system, as shown in Figure 1. In this coordinate system, the total wave function, ψ, can be expressed as the product of three functions, each of which is dependent only on one coordinate:

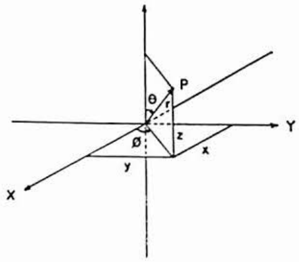

Figure 1. The Cartesian coordinates (x, y, z) and the spherical coordinates (r, θ, ϕ) of a point P.

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\cdot\Theta_{lm}(\theta)\cdot\Phi_m(\phi) \quad (1)$$

where n is the principle quantum number, l is the azimuthal quantum number, and m is the magnetic quantum number. The shapes of the orbitals are determined primarily by the angular part of ψ.

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\cdot\Phi_m(\phi) \quad (2)$$

Therefore, we are concerned principally with equations for Y in terms of θ and ϕ.

Each wave function must be normalized for comparison with other wave functions. This means that the constants in the expression for ψ must be adjusted so that

$$\int \psi^*\psi \, dv = \text{normalization factor} \quad (3)$$

where $dv = r^2 \sin\theta \, d\phi \, d\theta \, dr$ is the differential of volume, and the integration is taken over all space. ψ^* is the complex conjugate of ψ. In the case of real wave functions, such as those in this paper, $\psi^* = \psi$, and $\psi^*\psi = \psi^2$. The normalization factor is usually taken as 1 (e.g., Pauling) when the total wave function is being considered, or as 4π (e.g., Eisenstein) when only the angular part is being considered. In this work, the angular part and the radial part of the wave functions have been separately normalized to 1; i.e.,

$$\int_0^{\pi}\int_0^{2\pi} Y_{lm}^2(\theta, \phi) \sin\theta \, d\phi \, d\theta = 1$$

$$\int_0^{\infty} R_{nl}^2(r) \, r^2 \, dr = 1$$

The *f* orbitals are unusual in that no single set is equally useful in all problems. One set, which we shall call the *general set*, is obtained in the usual way, i.e., by forming the product $\Theta(\theta)\cdot\Phi(\phi)$. However, this set contains no orbitals which are triply-degenerate in the presence of a ligand field, and group theory predicts (*8*) that when *f* orbitals split in cubic type fields (cubic, tetrahedral, octahedral), they should split into two groups of triply-degenerate orbitals and one nondegenerate orbital. A second set of real *f* orbitals can be derived from the first (*8, 9*) by combining four of the orbitals in the general set to give four new orbitals, while the other three orbitals remain the same. This new set, which we shall call the *cubic set,* contains two groups of orbitals which are triply-degenerate in a ligand field, and consequently, is more useful in considering cubic-type fields. The general set is more useful in considering other fields (e.g., tetragonal, trigonal planar, etc.) where no more than double degeneracy is required. Both sets are equally valid, since orbitals (or wave functions) are essentially mathematical models of the square root of electron probability distribution, and both of these sets meet the mathematical criteria for valid wave functions equally well.[3] Therefore, whichever set is convenient to a given problem may be used.

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Table 1. Angular Parts of the *f* Orbitals (*7, 8*)

a. The general set

True polynomial	Simplified polynomial	$Y_{lm}(\theta, \phi)$
$z(5z^2 - 3r^2)$	z^3	$1/4\sqrt{7/\pi}\,(5\cos^3\theta - 3\cos\theta)$
$x(5z^2 - r^2)$	xz^2	$1/8\sqrt{42/\pi}\,\sin\theta\,(5\cos^2\theta - 1)\cos\phi$
$y(5z^2 - r^2)$	yz^2	$1/8\sqrt{42/\pi}\,\sin\theta\,(5\cos^2\theta - 1)\sin\phi$
$z(x^2 - y^2)$		$1/4\sqrt{105/\pi}\,\sin^2\theta\cos\theta\cos 2\phi$
xyz		$1/4\sqrt{105/\pi}\,\sin^2\theta\cos\theta\sin 2\phi$
$x(x^2 - 3y^2)$		$1/8\sqrt{70/\pi}\,\sin^3\theta\cos 3\phi$
$y(3x^2 - y^2)$		$1/8\sqrt{70/\pi}\,\sin^3\theta\sin 3\phi$

b. The cubic set

Bethe's notation	True polynomial	Simplified polynomial	$Y_{lm}(\theta, \phi)$
δ	$x(5x^2 - 3r^2)$	x^3	$1/4\sqrt{7/\pi}\,\sin\theta\cos\phi\,(5\sin^2\theta\cos^2\phi - 3)$
	$y(5y^2 - 3r^2)$	y^3	$1/4\sqrt{7/\pi}\,\sin\theta\sin\phi\,(5\sin^2\theta\sin^2\phi - 3)$
	$z(5z^2 - 3r^2)$	z^3	$1/4\sqrt{7/\pi}\,(5\cos^3\theta - 3\cos\theta)$
β	xyz	...	$1/4\sqrt{105/\pi}\,\sin^2\theta\cos\theta\sin 2\phi$
ε	$x(z^2 - y^2)$	...	$1/4\sqrt{105/\pi}\,\sin\theta\cos\phi\,(\cos^2\theta - \sin^2\theta\sin^2\phi)$
	$y(z^2 - x^2)$	...	$1/4\sqrt{105/\pi}\,\sin\theta\sin\phi\,(\cos^2\theta - \sin^2\theta\cos^2\phi)$
	$z(x^2 - y^2)$	...	$1/4\sqrt{105/\pi}\,\sin^2\theta\cos\theta\cos 2\phi$

Pictures of the *f* Orbitals

The *f* orbital pictures presented here consider only the angular part of the wave functions, and do not include the distortions produced by the radial part. The equations used are presented in Table 1 for both real sets of *f* orbitals. For the cubic set, Bethe's Greek letter notation is given; this corresponds to the familiar designations of the *d* orbitals as d_γ and d_ϵ.

The polynomials frequently used as subscripts in designating orbitals are properly derived by substituting in the function $Y(\theta, \phi)$

$$\sin\theta\cos\phi = x/r$$
$$\sin\theta\sin\phi = y/r$$
$$\cos\theta = z/r$$

and dropping the denominator, which is always a power of *r*. Some subscripts can be further reduced, for simplicity in notation, by dropping terms containing only *r*. Thus, the orbital usually designated as d_{z^2} is correctly designated $d_{3z^2-r^2}$ or, equally correctly, $d_{2z^2-x^2-y^2}$ (since $r^2 = x^2 + y^2 + z^2$). Similarly, several of the designations for *f* orbitals can be reduced for simplicity. Both the true and the simplified polynomial subscripts are shown in Table 1. In this paper, the simplified subscripts are always used.

The orbitals f_{x^3}, f_{y^3}, $f_{x(z^2-y^2)}$, and $f_{y(z^2-x^2)}$ of the cubic set are obtained by combining the f_{xz^2} and $f_{x(x^2-3y^2)}$, and the f_{yz^2} and $f_{y(3x^2-y^2)}$ orbitals of the general set:

$$\begin{aligned} f_{x^3} &= -1/4[\sqrt{6}\,f_{xz^2} - \sqrt{10}\,f_{x(x^2-3y^2)}] \\ f_{y^3} &= -1/4[\sqrt{6}\,f_{yz^2} + \sqrt{10}\,f_{y(3x^2-y^2)}] \\ f_{y(z^2-y^2)} &= 1/4[\sqrt{10}\,f_{xz^2} + \sqrt{6}\,f_{x(x^2-3y^2)}] \\ f_{y(z^2-x^2)} &= 1/4[\sqrt{10}\,f_{yz^2} - \sqrt{6}\,f_{y(3x^2-y^2)}] \end{aligned} \quad (5)$$

The other three *f* orbitals, f_{z^3}, f_{xyz}, and $f_{z(x^2-y^2)}$, are common to both sets.

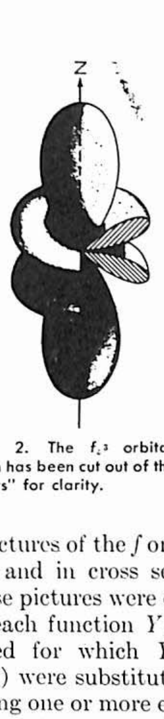

Figure 2. The f_{z^3} orbital. A section has been cut out of the two "collars" for clarity.

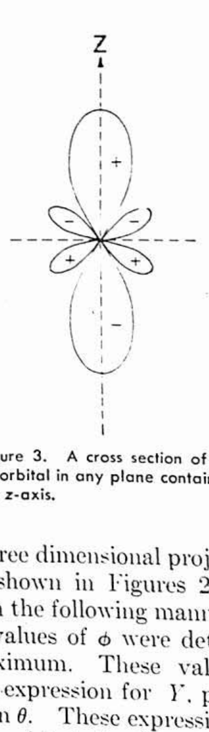

Figure 3. A cross section of the f_{z^3} orbital in any plane containing the *z*-axis.

Pictures of the *f* orbitals, in three dimensional projection and in cross section, are shown in Figures 2–8. These pictures were developed in the following manner: for each function $Y(\theta, \phi)$, the values of ϕ were determined for which *Y* is a maximum. These values ($\phi_{\max}$) were substituted into the expression for *Y*, producing one or more expressions in θ. These expressions represent cross sections of the orbitals in the planes corresponding to the values of $\phi_{\max}$ (e.g., the *xz*-plane corresponds to $\phi_{\max} = 0$ and the *yz*-plane corresponds to $\phi_{\max} = 90°$). These expressions were plotted on polar coordinate paper. Similarly, values of $\theta_{\max}$ were determined and used to plot other cross sections (e.g., the *xy*-plane corresponds to $\theta_{\max} = 90°$). Finally, the cross sections were used to construct the three-dimensional pictures. Figures 2–8 are all drawn to the same scale. The sign of the wave function in each lobe is indicated on the cross sections. For clarity, the signs are not shown on the three dimensional projections, but may be obtained by inspection of the cross sections and of the polynomial subscripts. (Adjacent lobes of the same orbital always have different signs.)

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[3] For example: both sets obey Unsold's theorem; all orbitals in each set are orthogonal to all others in the same set; etc.

Figure 2 shows a three-dimensional view of the f_{z^3} orbital, with a section cut out of the two "collars." Figure 3 is a cross section of the same orbital in any plane containing the z-axis. The f_{x^3} and f_{y^3} orbitals are identical, except that they extend along the x- and y-axes, respectively.

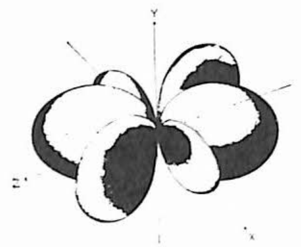

Figure 4. The f_{xz^2} orbital.

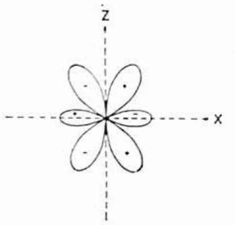

Figure 5. A cross section of the f_{xz^2} orbital in the xz-plane.

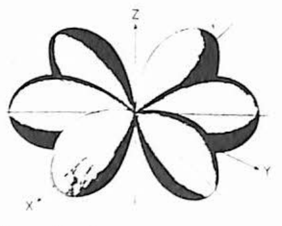

Figure 6. The $f_{x(x^2-3y^2)}$ orbital.

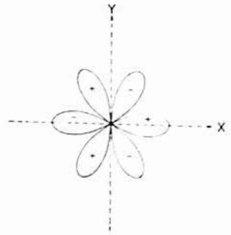

Figure 7. A cross section of the $f_{x(x^2-3y^2)}$ orbital in the xy-plane.

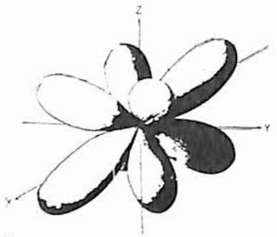

Figure 8. The f_{xyz} orbital.

Figure 4 is a three-dimensional view of the f_{xz^2} orbital, and Figure 5 is the cross section of this orbital in the xz-plane. The f_{yz^2} orbital is identical in shape, but is rotated 90° around the z-axis, so that the axis of the small lobes (the horizontal axis in Fig. 5) is the y-axis. The cross section of each lobe of these orbitals, in a plane perpendicular to that of Figure 5 and passing through the nucleus, is a circle. As a result, these lobes appear flattened, resembling a lima bean.

A three-dimensional view of the $f_{x(x^2-3y^2)}$ orbital is shown in Figure 6, and a cross sectional view (the xy-plane) in Figure 7. The $f_{y(3x^2-y^2)}$ orbital is the same shape, being formed by rotating the lobes of Figures 6 and 7 about the z-axis 90° clockwise. All six lobes of each orbital are identical. The cross section of each lobe in any plane perpendicular to the axis of the lobe is elliptical.

The f_{xyz} orbital, shown in Figure 8, has eight identical lobes which point toward the corners of a cube whose center is at the nucleus. The $f_{x(z^2-y^2)}$, $f_{y(z^2-x^2)}$, and $f_{z(x^2-y^2)}$ orbitals are the same shape, but are rotated 45° about the x-, y-, and z-axes, respectively.

Ligand Field Splitting of f Orbitals

It was stated earlier that group theory predicts that in a cubic-type ligand field, the f orbitals should split into two groups of triply-degenerate orbitals and one nondegenerate orbital. Knowing the shapes and orientations of the f orbitals, we may now consider their behavior in three fields: the octahedral and tetrahedral (cubic-type fields), and the hexagonal bipyramidal.[1]

Consider six ligands arranged in a regular octahedron, as shown in Figure 9. It is seen that the ligands are also in the centers of the faces of a cube circumscribed about the octahedron. The three groups of f orbitals whose relative energies we must consider are the f_β, f_δ, and f_ϵ orbitals (see Table 1*b*). It can be seen readily (*9*) that the f_δ orbitals point directly toward the ligands, and so are of highest energy; the f_ϵ point toward the centers of the edges of the cube, and so are of lower energy than f_δ; and f_β points toward the corners of the cube, and so is of lowest energy. This is shown on the left in Figure 10, in which the energy differences are designated by Δ and θ.

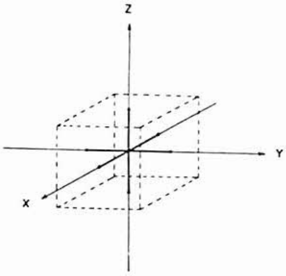

Figure 9. Six ligands arranged in a regular octahedron, showing the cube circumscribed about the octahedron.

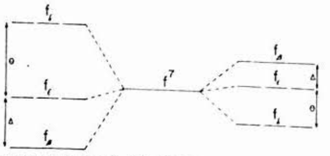

Figure 10. Splitting of the f orbitals in octahedral and tetrahedral ligand fields.

The tetrahedron is most simply considered as being a cube with a ligand at every other corner (Fig. 11). The same type of reasoning as for the octahedron leads to the conclusion that f_β is of highest energy, f_ϵ of lower energy, and f_δ of lowest energy. This is shown on the right in Figure 10.

For the hexagonal bipyramid, group theory predicts (*10*) that the f orbitals will split into two pairs of doubly-degenerate orbitals and three nondegenerate orbitals. Since the highest degeneracy is double, we use the general set of f orbitals. For convenience, we shall number them for this problem as shown in the first two columns of Table 2. The hexagonal bipyramid is formed as shown in Figure 12 by arranging six ligands in a hexagon in the xy-plane, and putting the other two ligands on the z-axis above and below the hexagon. It can be seen that the f_1 orbital points directly toward the two z-axis ligands and f_2 points toward the six xy-plane ligands, so these must be of highest energy. On the other hand, the two f_5 orbitals point away from all eight ligands, and therefore must be of lowest energy. The f_3 orbital points between the ligands in the xy-plane, so it must be low in energy. Finally, the f_4 orbitals point toward some of the ligands, but do not extend very far directly toward any of them; these must be raised only slightly in energy. These considerations are summarized in Figure 13. A possible example of this arrangement is the complex $UO_2(NO_3)_3^-$ and other complexes of the uranyl ion. These are discussed in detail by Coulson and Lester (*10*).

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[1] The symmetry species of the f orbitals in the three fields are given in Table 2 since they are frequently used as designations for the orbitals in molecular orbital and ligand field discussions. However, Table 2 is not necessary to the discussion which follows.

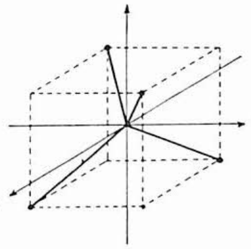

Figure 11. Four ligands arranged in a regular tetrahedron, shown as a cube with a ligand at every other corner.

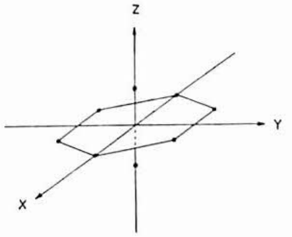

Figure 12. Eight ligands arranged in a hexagonal bipyramid. Six ligands are at the corners of a hexagon in the xy-plane. The other two are on the z-axis above and below the xy-plane.

Table 2. Symmetry Species of the f Orbitals in Various Fields

Octahedron point group O_h		Tetrahedron point group T_d	
f_β	a_{2u}	f_β	a_1
f_δ	t_{1u}	f_δ	t_2
f_ϵ	t_{2u}	f_ϵ	t_1
Hexagonal bipyramid point group D_{6h}			
f_1	f_{z^3}	a_{2u}	
f_2	$f_{x(x^2-3y^2)}$	b_{1u}	
f_3	$f_{y(3x^2-y^2)}$	b_{2u}	
f_4	f_{xz^2}, f_{yz^2}	e_{1u}	
f_5	$f_{xyz}, f_{z(x^2-y^2)}$	e_{2u}	

We have discussed here only the manner in which the f orbitals split in a given ligand field, but have said nothing about the amount of splitting. In the lanthanides, this splitting is very slight, probably not more than about 10% (*3*).

Radial Part of the f Orbitals

The radial part of the f orbitals is interesting principally in comparing the size of the f orbitals and the outermost occupied orbitals of a given atom. Of particular importance for the lanthanide elements is a comparison of the $4f$ orbitals with the $5d$ and $6s$ valence orbitals. For this purpose, we have used the hydrogenic radial functions, $R_{nl}(r)$, as applied to cerium, the first member of the lanthanide series. This is only an approximation, principally because the interactions between electrons are ignored in the hydrogenic radial functions. Furthermore, the functions have been calculated for the neutral atom, not for the trivalent ion. K. Rajnak (*11*) has calculated more precise radial functions for the ions Pr^{3+} and Tm^{3+} from the self-consistent field calculations of E. C. Ridley (*12*). These functions are qualitatively similar to the hydrogenic functions used in this discussion.

The hydrogenic radial functions of cerium give us a qualitative picture of the $4f$ orbitals at the beginning of the lanthanide series. This is indicated in Figure 14, in which the probability, $4\pi r^2 R_{nl}^2$, of finding an electron at the distance r from the nucleus is plotted as a function of r for the $4f$, $5d$, and $6s$ orbitals of cerium. The region in which the $4f$ orbitals are important is seen to be deep within the atom, compared to the $5d$ and $6s$ orbitals. Indeed, the $5s$ and $5p$ orbitals, which are not valence electrons in the lanthanides, extend out beyond the $4f$ and about as far as the $5d$. Thus, it can be understood qualitatively why the $4f$ orbitals do not participate in bonding in the lanthanide series to any great degree. These orbitals are unavailable spatially, not energetically, as they simply do not extend out far enough to join in bonding to any appreciable extent. Similarly, they are so well shielded that they are not greatly affected by ligand fields, and so do not split appreciably.

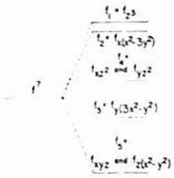

Figure 13. Splitting of the f orbitals in a hexagonal bipyramidal ligand field.

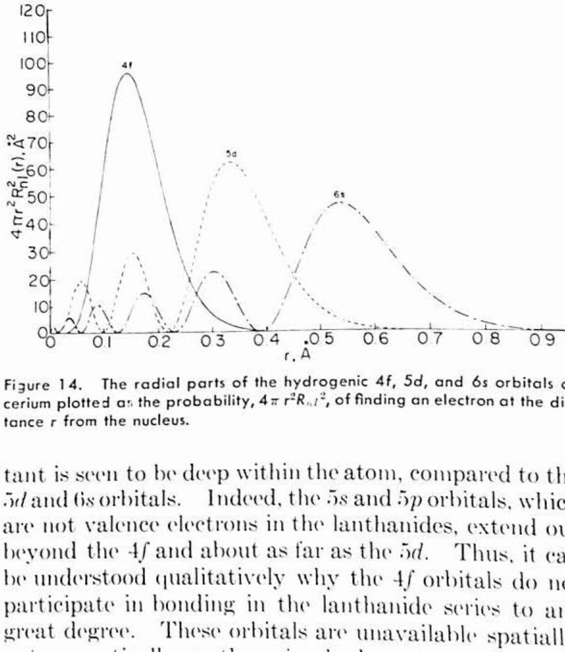

Figure 14. The radial parts of the hydrogenic 4f, 5d, and 6s orbitals of cerium plotted as the probability, $4\pi r^2 R_{nl}^2$, of finding an electron at the distance r from the nucleus.

Acknowledgment

It is a pleasure to acknowledge helpful discussions with Professors M. Kasha and B. Linder. We are also grateful to Mr. R. Woodward for advice on the construction of the figures, and to the U.S. Atomic Energy Commission for financial support.

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Geometry of the *f* Orbitals

EDITOR'S NOTE: The coincidence of receiving two articles on the same theme at the same time justifies mention. Mr. Becker has shown consideration for editor and reader by modifying his original manuscript by drastic reduction to avoid obvious repetition. The subtle differences in the two presentations here provided (e.g., the choice of normalization factor and the choice of axis designations) should serve as a focus rather than a dispersion of reader interest. The comparison of figures should also add to the reader's interst and understanding.

Models of atomic orbitals obtained from the angular portions $[Y(\theta,\phi)]$ of the hydrogenic wave functions $[\psi(r,\theta,\phi)]$ have been very useful in understanding the geometry of chemical bonds. A geometric representation of an orbital, however, usually conveys a physical significance of probability distribution of an electron. The probability of finding an electron in a particular space is given as: $\int \psi^2(r\theta\phi)dV$, or in this consideration, $\int\int Y^2(\theta\phi) \sin\theta d\phi d\theta$, where the probability is associated with the square of the amplitude of the wave function.[2]

Approximate orbital representations can be achieved by graphing characteristic cross sections of the squared angular functions; the Styrofoam models pictured in this article are based on such graphs. The spherical coordinates used for these functions are defined by Figure 1.[3]

Table 1. Angular Functions of the *f* Orbitals

$$Y_{x(x^2-3y^2)} = \frac{1}{4}(70)^{1/2}\sin^3\theta\cos 3\phi \tag{A}$$
$$Y_{y(3x^2-y^2)} = \frac{1}{4}(70)^{1/2}\sin^3\theta\sin 3\phi \tag{B}$$
$$Y_{z(5z^2-3r^2)} = \frac{1}{2}(7)^{1/2}(5\cos^3\theta - 3\cos\theta) \tag{C}$$
$$Y_{x(5z^2-r^2)} = \frac{1}{4}(42)^{1/2}\sin\theta(5\cos^2\theta - 1)\cos\phi \tag{D}$$
$$Y_{y(5z^2-r^2)} = \frac{1}{4}(42)^{1/2}\sin\theta(5\cos^2\theta - 1)\sin\phi \tag{E}$$
$$Y_{(x^2-y^2)z} = \frac{1}{2}(105)^{1/2}\sin^2\theta\cos\theta\cos 2\phi \tag{F}$$
$$Y_{xyz} = \frac{1}{2}(105)^{1/2}\sin^2\theta\cos\theta\sin 2\phi \tag{G}$$

The angular distribution functions[4] for the *f* orbitals normalized to 4π (Table 1) describe four basic orbital

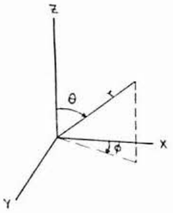

Figure 1.

Delivered in part at an ACS Undergraduate Chemistry Symposium held at Macalester College, St. Paul, Minnesota, April 27, 1963.

The author gratefully acknowledges the guidance and encouragement of Professors James A. Ryan and James J. Carney.

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[2] DAY, M. CLYDE, JR., AND SELBIN, JOEL, "Theoretical Inorganic Chemistry," Reinhold Publishing Corp., New York, 1962, p. 32.

[4] EISENSTEIN, J. C., *J. Chem. Phys.*, 25, 142 (1956).

[3] Editor's Note: The reader who is making comparisons with the accompanying article by FRIEDMAN, H. G., CHOPPIN, G. R., and FEUERBACHER, D. G., THIS JOURNAL, 41, 354 (1964) should note the difference in definition of coordinate systems. Rather than change one or the other set of designations, the correlation of the two representations remains as an "exercise for the reader." For example, Becker's $f_{y(5z^2-r^2)}$ is the Friedman, Choppin, and Feuerbacker $f_{x(5z^2-r^2)}$, also designated as f_{xz^2}.

shapes. The photographs in Figures 3–10 show Styrofoam models of the Y^2 functions for the orbitals described in Table 1. (A) and (B) give complementary six-lobed lemniscates in the xy-plane, i.e., $(\cos 3\phi)^2$ and $(\sin 3\phi)^2$, with (A) projecting lobes along the x-axis but none in the yz-plane (Fig. 3), while the xz-plane is nodal for (B) and two of (B)'s lobes are directed along the y-axis (Fig. 4). As a second cross section, taken perpendicular to the xy-plane, e.g., $\phi = 0°$ or $\phi = 90°$, the nonsuperimposable $(\sin^3 \theta)^2$ is obtained, making the individual lobes rather flattened. These orbitals are concentrated in the region of the xy-plane and have no projection along the z-axis (maximum magnetic quantum number).

(C), (Fig. 5), exhibits the trace $(5 \cos^3 \theta - 3 \cos \theta)^2$ in all planes passing through the z-axis since it is independent of ϕ. Figure 2 shows the graphs of these for Y and Y^2. The xy-plane is nodal, and the function becomes zero for $\theta = 39°14'$, $90°$, $140°46'$, $219°14'$, $270°$, and $320°46'$, gives relative maxima for $\theta = 64°$, $116°$, $244°$, and $296°$, and absolute maxima for $\theta = 0°$, $180°$ (z-axis) for all ϕ. The orbital representation of $f_{z(5z^2-3r^2)}$, as based on $Y^2_{z(5z^2-3r^2)}$, appears rather analogous to that of d_{z^2} (Fig. 6) since both are concentrated along the z-axis and are independent of ϕ (zero magnetic quantum number).

$|\text{Sin}\, \theta\, (5 \cos^2 \theta - 1)|^2$ is the principal section for (D) in the xz-plane ($\phi = 0°$) (Fig. 7) and for (E) (Fig. 8) in the yz-plane ($\phi = 90°$), while (D) has no projection in the yz-plane and (E) no projection in the xz-plane. The principal section exhibits zeros for $\theta = 0°$, $63.5°$, $116.5°$, $180°$, $243.5°$, and $296.5°$, and relative maxima

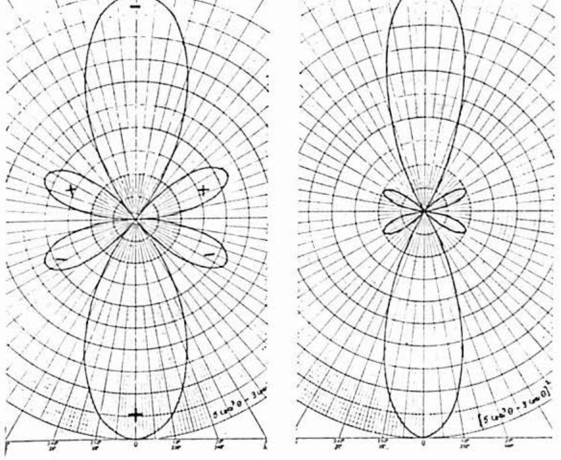

Figure 2. Graphs of the xz and yz cross sections of the angular function for $f_{z(5z^2-3y^2)}$ (left) and the squared angular function (right).

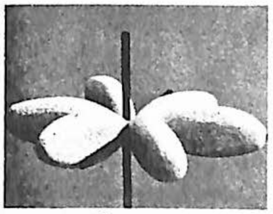

Figure 3. Y^2 model of $f_{x(x^2-3y^2)}$.

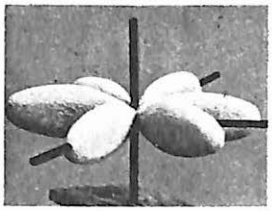

Figure 4. Y^2 model of $f_{y(3x^2-y^2)}$.

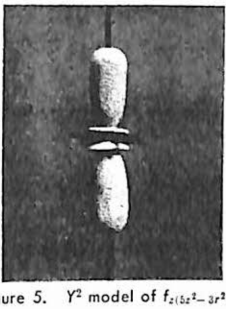

Figure 5. Y^2 model of $f_{z(5z^2-3r^2)}$.

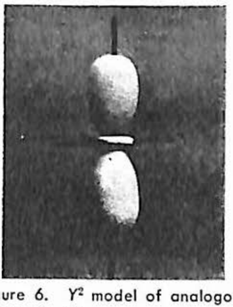

Figure 6. Y^2 model of analogous 3d orbital, d_{z^2}.

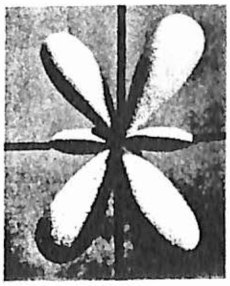

Figure 7. Y^2 model of $f_{x(5z^2-r^2)}$.

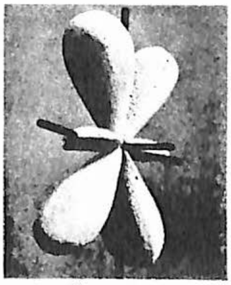

Figure 8. Y^2 model of $f_{y(5z^2-r^2)}$.

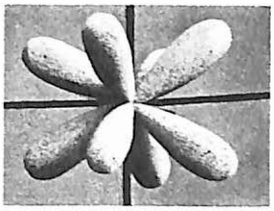

Figure 9. Y^2 model of $f_{(x^2-y^2)z}$.

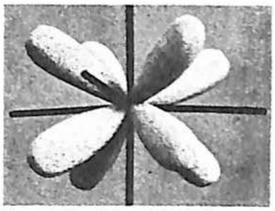

Figure 10. Y^2 model of f_{xyz}.

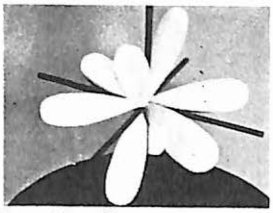

Figure 11. Y^2 model of $f_{(z^2-y^2)x}$.

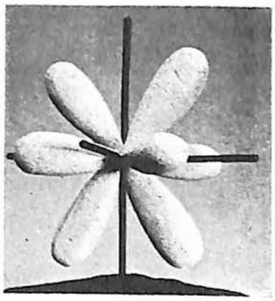

Figure 12. Y^2 model of $f_{(z^2-x^2)y}$.

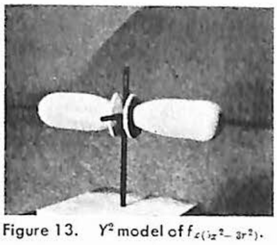

Figure 13. Y^2 model of $f_{x(5x^2-3r^2)}$.

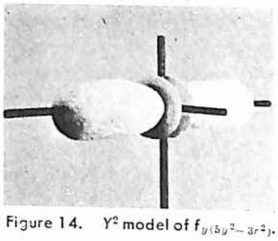

Figure 14. Y^2 model of $f_{y(5y^2-3r^2)}$.

for $\theta = 31°$, $90°$, $149°$, $211°$, $270°$, and $329°$, for the appropriate constant ϕ. A cross section taken perpendicular to the smaller lobes at $\theta = 90°$, i.e., in the xy-plane, is $(\cos\phi)^2$, but the oblique cross section of the larger lobes for $\theta = 31°$ is an approximated $(\cos^2\phi)^2$ since this section cannot be taken directly. These rather flat orbitals are confined to the regions of the xz- and yz-planes respectively.

(F), (Fig. 9), exhibits the cross section $(\sin^2\theta\cos\theta)^2$ with unsymmetrical lobes in both the xz- and yz-planes, while (G), (Fig. 10), is nodal for these planes, but gives that function for $\phi = 45°$ and $135°$. Maxima are observed for $\theta = 54°44'$, $125°16'$, $234°44'$, and $305°16'$ in their respective planes, and the function zeros occur on the axes, i.e., for $\theta = 0°$, $90°$, $180°$, and $270°$, and also for $\phi = 45°$ and $135°$ for (F) and $\phi = 0°$ and $90°$ for (G). The maximum cross sections perpendicular to the major section can only be estimated. The more widely separated adjacent lobes interestingly exhibit the tetrahedral angle $109°28'$. (F) and (G) are the first eight-lobed atomic orbitals encountered.

An alternate set of f orbitals, especially applicable to cubic systems, is also sometimes listed.[4] In this set, f_{β}, f_{δ_1}, and f_{ϵ_1} are identical with f_{xyz}, $f_{z(5z^2-3r^2)}$, and $f_{(x^2-y^2)z}$ respectively; $f_{x(5x^2-3r^2)}$ or f_{δ_2} and $f_{y(5y^2-3r^2)}$ or f_{δ_3} have shapes equivalent to $f_{z(5z^2-3r^2)}$ but are located along the x and y axes respectively; and $f_{(z^2-y^2)x}$, i.e. f_{ϵ_2}, and $f_{(x^2-z^2)y}$ or f_{ϵ_3} have shapes equivalent to $f_{(x^2-y^2)z}$, but project their lobes about the y and z axes and x and z axes respectively. Both sets of f orbitals are found useful.

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THE PERIODIC TABLE AS A TEACHING AID

by

E. Pachmann[1], R. Palous[1], A. Schutz[2]

All teaching aids can be divided into two groups, one including aids designed to bring a subject in question (e.g. a mineral or a chemical) as a real thing into the classroom, as close to the student as possible, the other including teaching aids which make it easier for a student to understand the true origin of a property, of an effect, or of a natural law and to develop in him at the same time a scientific way of thinking. A typical example of a teaching aid of the second type is the periodic table of the elements.

When considering the periodic table as a teaching aid, its twofold purpose at the primary, secondary, as well as university school level should be mentioned: 1) It may be used as a tabular summary of some important properties of the elements (symbols, atomic numbers, atomic weights, as well as melting points, thermal or electrical conductivities etc.) designed for a

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quick reference and for finding out the values of these constants rather than for illustrating the periodic law.

In this article we will concentrate on the first of these two points of view. Yet, in discussing this point we do not intend to deal with such questions as, for example, what difference there should be between a periodic table as a chart and a text-book periodic table, or what prospects there are of using periodic table forms to be filled in by the students themselves, or what may be expected from introducing sets of transparent periodic tables to be laid on each other. Thus, there remains only one important aspect to be discussed in this article, namely: What kind of graphic means seems to be most suitable for making out of a periodic table an easily comprehensible and very illustrative graphic representation of the periodic law.

Before trying to answer this question, we should state to what use the explanations connected with the periodic law may be put in the teaching of Chemistry. In this sense, the periodic law seems to be a logical conclusion resulting from a display of experimental information about the elements and about the structures of their atoms. At first, the students should realise that there is some relation between the chemical properties of the elements and the structure of their atoms, the next step being an attempt to find a way of formulating this relation. This cannot be done properly, unless two quantities representing the electron structure of an atom and the chemical property of a corresponding element, respectively, are defined. After having defined them, the relation between the chemical properties and the atomic structures of the elements could be plotted as a simple xy-graph, so as to see what this relation looks like and whether a generalised law concerning this relation can be formulated.

In order to do this, proper ways have to be found of expressing the electron structures of atoms and the chemical properties of the elements, and it is here that the suitability of a graphic presentation must be kept in mind.

The simplest (but not very complete) information about the electron structure of an atom is, beyond all doubt, the number of electrons possessed by the electroneutral atom, i.e. the atomic number Z. In spite of the incompleteness of this information one real advantage of it must be considered: it is suitable for plotting

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its values on the x-axis of a simple xy-graph. If the values of any quantity, sufficiently expressing the chemical properties of the elements, are plotted against Z values of various elements, a kind of periodicity of the chemical properties in the natural row of elements can be easily demonstrated. It is important to realise that even this very primitive graphic representation of the relation atomic structure - chemical property makes it possible to formulate the periodic law in the well-known form: "In the natural row of elements the chemical properties change in a periodic manner with the increasing atomic number." Nevertheless, no pupil will be able to understand why this periodicity exists and of what use the periodic law can be for a chemist.

To improve this, more complete information has to be used about the electron structures of atoms - namely their electron configurations, stating how the electrons are distributed among the orbitals. Unfortunately, this more complete information is not suitable for plotting on the x-axis, as it consists of a set of data, showing the total number of electrons in each of the groups of orbitals (e.g. 1s, 2s, 2p etc.). Nevertheless, it is possible to by-pass the need for a multidimensional graphic presentation of the electron configurations of atoms. We can avail ourselves of the fact that in most cases the electron configuration of an atom can be derived by adding one extra electron to the electron configuration of the atom of the element just preceding it in the natural row of elements. Thus, if only the orbital of this added electron is given for each of the elements, the entire electron configuration can be easily constructed (provided the exceptions are properly indicated).

Consequently, it is possible to design a diagram (Fig. 1) each frame of which represents one place for an electron available within a set of orbitals, this set being marked by the principal quantum number (left) and by the symbol s, p, d, f (on the bottom). Now, the symbols of the elements can be written into these frames according to the orbital that accommodated the last electron of the atom of the given element (the number of electrons already present in the given set of orbitals being respected at the same time); e.g. fluorine occupies the 7th frame of the 2nd row, because its electron configuration differs from that of oxygen merely by the 7th electron in the 2p orbital set. However, some irregularities appear here, arising from the fact that some of the atoms differ from those preceding them by more than one electron (two, exceptionally three) in a d-orbital or f-orbital, having lost one electron (exceptionally two electrons) in the higher s-orbital or d-orbital, respectively, at the same time. This can be marked by an arrow directed from the frame, in which the symbol of the element should normally be located, to the frame where it actually is, due to the number of electrons in the orbitals in question; e.g. the niobium atom has two electrons more in its 4d-orbitals (but- at the same time - one electron less in its 5s-orbitals) than a zirconium atom.

Thus, we have obtained a two dimensional diagram (Fig.1) in which the electron configurations of all existing neutral atoms are represented and systematically arranged. The only question now is how to coordinate the chemical properties with these configurations. Obviously, it would not be very convenient for school charts or for text-books to make use of the third dimension for this purpose. Furtunately, there are other graphic means available, to be discussed later on.

The arrangement of elements (or preferably, of their atoms) shown in Fig. 1 is not the one we are very familiar with. Still, it may be constructed by the students themselves strictly in accordance with the table of electron configurations of atoms and, moreover, it shows clearly that all the elements can be divided into three major groups according to their electron configurations (elements of the principal groups - s+p; transition elements - d; inner transition elements - f). These groups can be seen very distinctly in this arrangement, so that the student will be able to find them and to distinguish them afterwards in any other rearrangement of this diagram. However, the periodic law in the formulation mentioned above may not stand out very clearly from this arrangement, only the fact that the chemical properties of the elements depend on the electron configurations of their atoms being demonstrated satisfactorily. It may be found, however, that some modification is necessary so as to make full use of both educational functions of the periodic table.

The most logical rearrangement of the diagram seems to be the one resulting from splitting the first major group (s+p) into two parts (s and p), so as to make it possible to locate the rows of transition elements between these two parts and thereby to restore the natural atomic consequence in the diagram. The same could be done with the inner-transition elements, locating them between the first and second columns of the transition elements (unless it is more convenient - in order to make the whole diagram shorter in size - to leave the innertransition elements as an extra part outside the table).

From this point of view a super-long arrangement of the table as well as the long arrangement (with only the inner-transition elements outside the framework of the table - Fig. 2) might be considered as most natural and most illustrative. Also, the rational arrangement suggested recently by Sanderson[2] (Fig. 3) seems to have some advantages from the educational point of view, as there is present here a simple and compact eight-group table to start with. On the other hand, the short arrangement (Fig. 4) is more suitable as a table of characteristic constants of the elements than as a teaching aid to illustrate the periodic law.

We suppose that this variety of possible graphic arrangements of the periodic table is quite sufficient to differentiate the groups of elements according to their atomic structures quite clearly. Differentiation by means of a colour code need not be introduced here, thus making it possible to save the colour code for other purposes in the periodic table.

Having constructed the two dimensional network of atomic structures, chemical properties should be introduced into it by means of a properly selected or defined quantity.

By this very requirement (i.e. a quantity is required, not merely a characteristic property to be estimated qualitatively) some of the characteristics used in the past frequently have to be ignored (e.g. the nature of the compounds containing hydrogen, oxygen, or chlorine was such a qualitative characterisation). Somewhat better prospects might be expected from the concept of ionisation potentials which is taken by Remy[3] for "being of decisive importance in the consideration of the chemical behaviour of elements". As a matter of fact, there are no troubles involved in teaching the concept of ionisation potentials, even at the secondary school level.

However, ionisation potential data concern only one aspect of the behaviour of an atom, the other aspect - electron affinity - being neglected. This may turn out to be rather unpleasant sometimes (it might lead, for instance, to the erroneous idea that oxygen and hydrogen are chemically similar since the values of their ionisation potentials are not very different). For these, and analogous reasons, electro-negativity seems to be the quantity that is most suitable for the characterisation of the general chemical behaviour of an element. According to Mulliken[4], electronegativity M_A of an atom should be defined as the arithmetical mean of its electron affinity E_A and its ionisation potential I_A, i.e. $M_A = \frac{1}{2}(E_A + I_A)$. This definition has the advantage of being simple enough to be understood properly by the secondary school students. (The same level of knowledge and experience as needed for the ionisation potentials concept is quite sufficient here.)

Now, the question of how the electronegativity values should be introduced into the periodic table, arises. The most comfortable, but not very effective, way is to put the values down, in figures, in the corresponding frames. However, this would not be a graphic representation of the periodic law, but merely a semigraphic one. If we wish to make the graphic representation as illustrative as possible and yet to maintain the two-dimensional form of the periodic table, only one way remains of expressing the electronegativity values - a colour code. The colour code seems to be particularly useful in that it presents a dynamic picture of the growth of electronegativity values in the table.

In Fig. 2 we have made use of two principal colours, yellow and red, and by mixing them in the appropriate ratios a nearly continuous colour scale can be obtained.* In Fig. 3 three principal colours may be used, much the same as Sanderson[1] used for painting his three-dimensional models of atoms (blue-yellow-red). But unlike Sanderson's scale, we use a red colour for high electro-negativity values and blue for the low ones to remind us of some of the earlier arrangements (blue-red, according to the acidity or basicity of the oxides of elements) which might still be seen by the students. A possible confusion of the two characterisations is prevented by use of yellow colour for the middle electro-negativity values.

In Fig. 3 the inconvenience of the shape and of the graphic arrangement of the table has to be made up for by means of greater variety of colours (a spectrum-like colour scale being used here). The evidence of periodicity can be maintained here only if the electro-negativities of the transition and inner transition elements are ignored. These two groups of elements are then presented in two grey shades, the one used for the inner transition elements being more intense than the other.

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*Editor's Note: In the original manuscript, Figures 2, 3 and 4 were hand coloured. The authors' descriptions have been retained in the text, but no attempt has been made to reproduce the colours.

In general, a colour scale should be designed for this purpose, to differentiate between electro-negativity values less than 0.3 units apart, otherwise the differences between the elements, e.g. between alkali metals or alkaline earths, respectively, may not be apparent in the table. So as to present the dynamic growth of electro-negativity values as clearly as possible within the colour scheme available, it would be convenient to arrange the colour scale in such a way, that the shades do not change quite uniformly within the scale, i.e. the colour fields in the lower part of the colour scale (0 - 2.3) should be narrower. In this way slight variations in electro-negativity values would be more apparent.

In this article we have tried to show, how the periodic table can be used not only to provide a graphic demonstration of the periodic law but also as a very effective tool to enable the students themselves to derive and understand this law. In our opinion, the way of representing the electron configurations by the location of the symbols of the elements in the two-dimensional diagram (of the long sort) as well as by expressing the chemical properties of an element by its electro-negativity value, the latter being colour coded (in addition to the numerical values), may be considered as most suitable for educational purposes.

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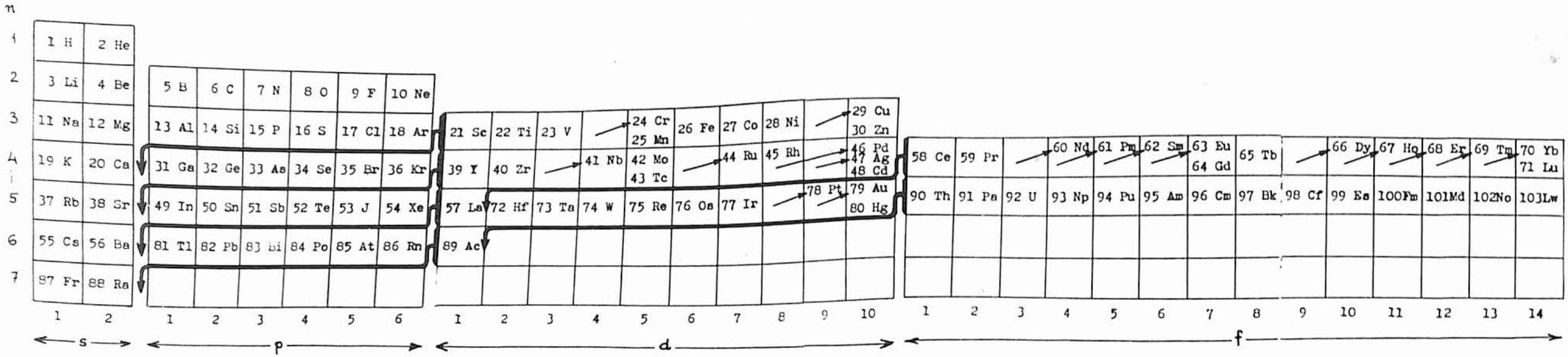
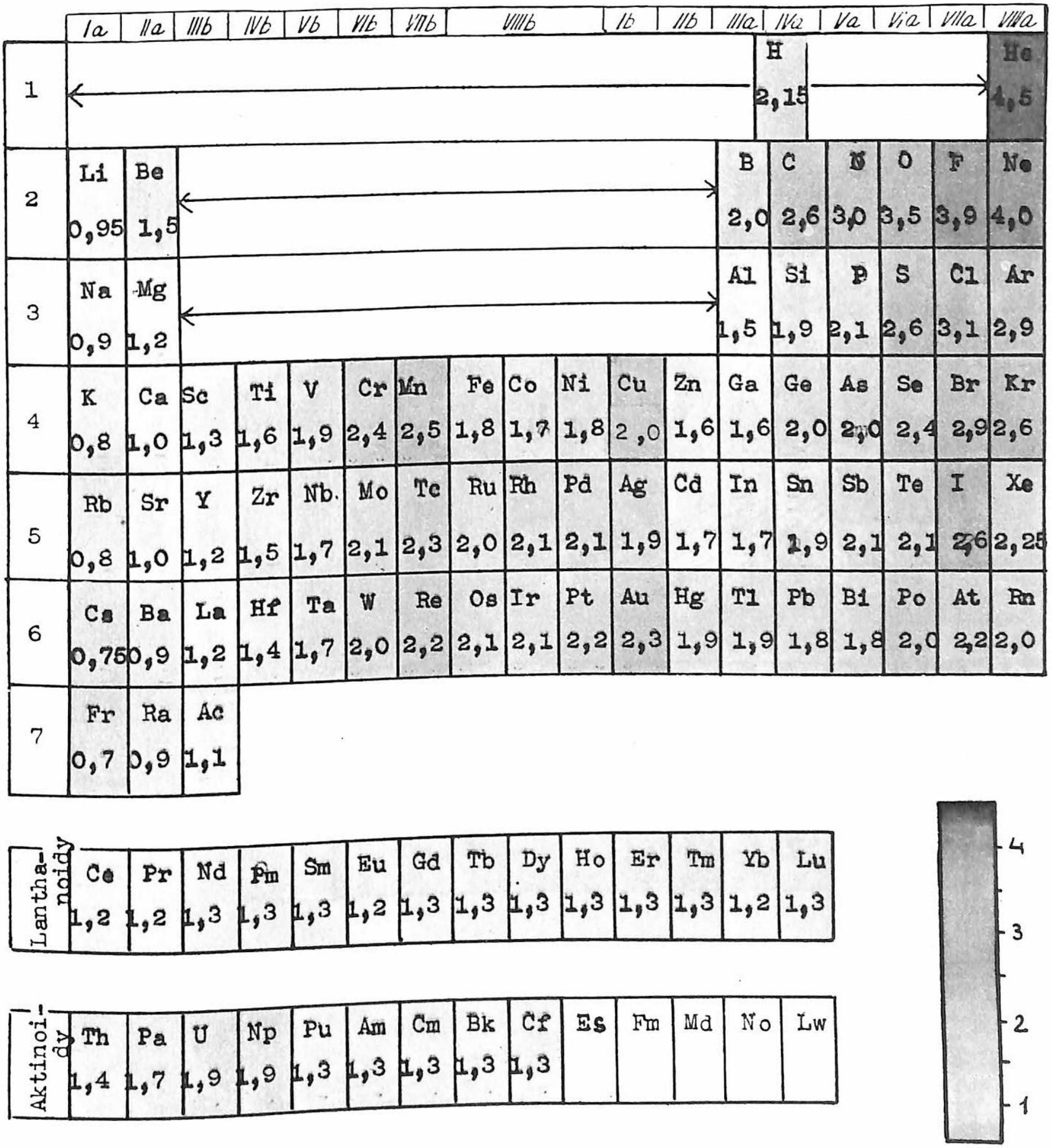
Fig 1

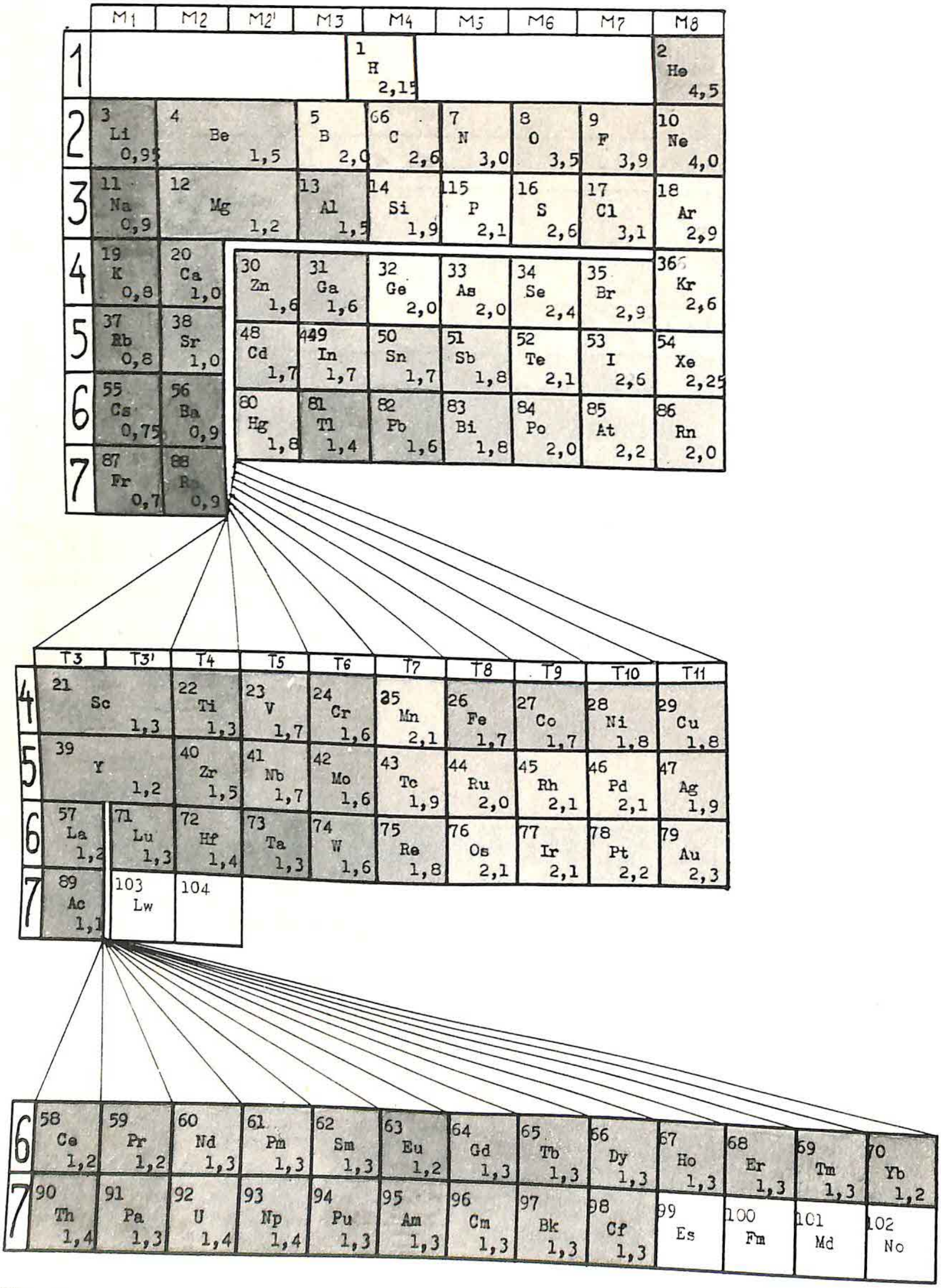

n
1
2
3
4
5
6
7
1 H
2 He
3 Li
4 Be
11 Na
12 Mg
19 K
20 Ca
37 Rb
38 Sr
55 Cs
56 Ba
87 Fr
88 Ra
5 B
6 C
7 N
8 O
9 F
10 Ne
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
49 In
50 Sn
51 Sb
52 Te
53 J
54 Xe
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
57 La
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
89 Ac
58 Ce
59 Pr
60 Nd
61 Pm
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100Fm
101Md
102No
103Lw
1 2
s
1 2 3 4 5 6
p
1 2 3 4 5 6 7 8 9 10
d
1 2 3 4 5 6 7 8 9 10 11 12 13 14
f



	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIIIb			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	VIIIa
1														H 2,15				He 4,5
2	Li 0,95	Be 1,5											B 2,0	C 2,6	N 3,0	O 3,5	F 3,9	Ne 4,0
3	Na 0,9	Mg 1,2											Al 1,5	Si 1,9	P 2,1	S 2,6	Cl 3,1	Ar 2,9
4	K 0,8	Ca 1,0	Sc 1,3	Ti 1,6	V 1,9	Cr 2,4	Mn 2,5	Fe 1,8	Co 1,7	Ni 1,8	Cu 2,0	Zn 1,6	Ga 1,6	Ge 2,0	As 2,0	Se 2,4	Br 2,9	Kr 2,6
5	Rb 0,8	Sr 1,0	Y 1,2	Zr 1,5	Nb. 1,7	Mo 2,1	Tc 2,3	Ru 2,0	Rh 2,1	Pd 2,1	Ag 1,9	Cd 1,7	In 1,7	Sn 1,9	Sb 2,1	Te 2,1	I 2,6	Xe 2,25
6	Cs 0,75	Ba 0,9	La 1,2	Hf 1,4	Ta 1,7	W 2,0	Re 2,2	Os 2,1	Ir 2,1	Pt 2,2	Au 2,3	Hg 1,9	Tl 1,9	Pb 1,8	Bi 1,8	Po 2,0	At 2,2	Rn 2,0
7	Fr 0,7	Ra 0,9	Ac 1,1															

Lantha-noidy	Ce 1,2	Pr 1,2	Nd 1,3	Pm 1,3	Sm 1,3	Eu 1,2	Gd 1,3	Tb 1,3	Dy 1,3	Ho 1,3	Er 1,3	Tm 1,3	Yb 1,2	Lu 1,3
Aktinoi-dy	**Th 1,4**	**Pa 1,7**	**U 1,9**	**Np 1,9**	**Pu 1,3**	**Am 1,3**	**Cm 1,3**	**Bk 1,3**	**Cf 1,3**	**Es**	**Fm**	**Md**	**No**	**Lw**

Fig. 2

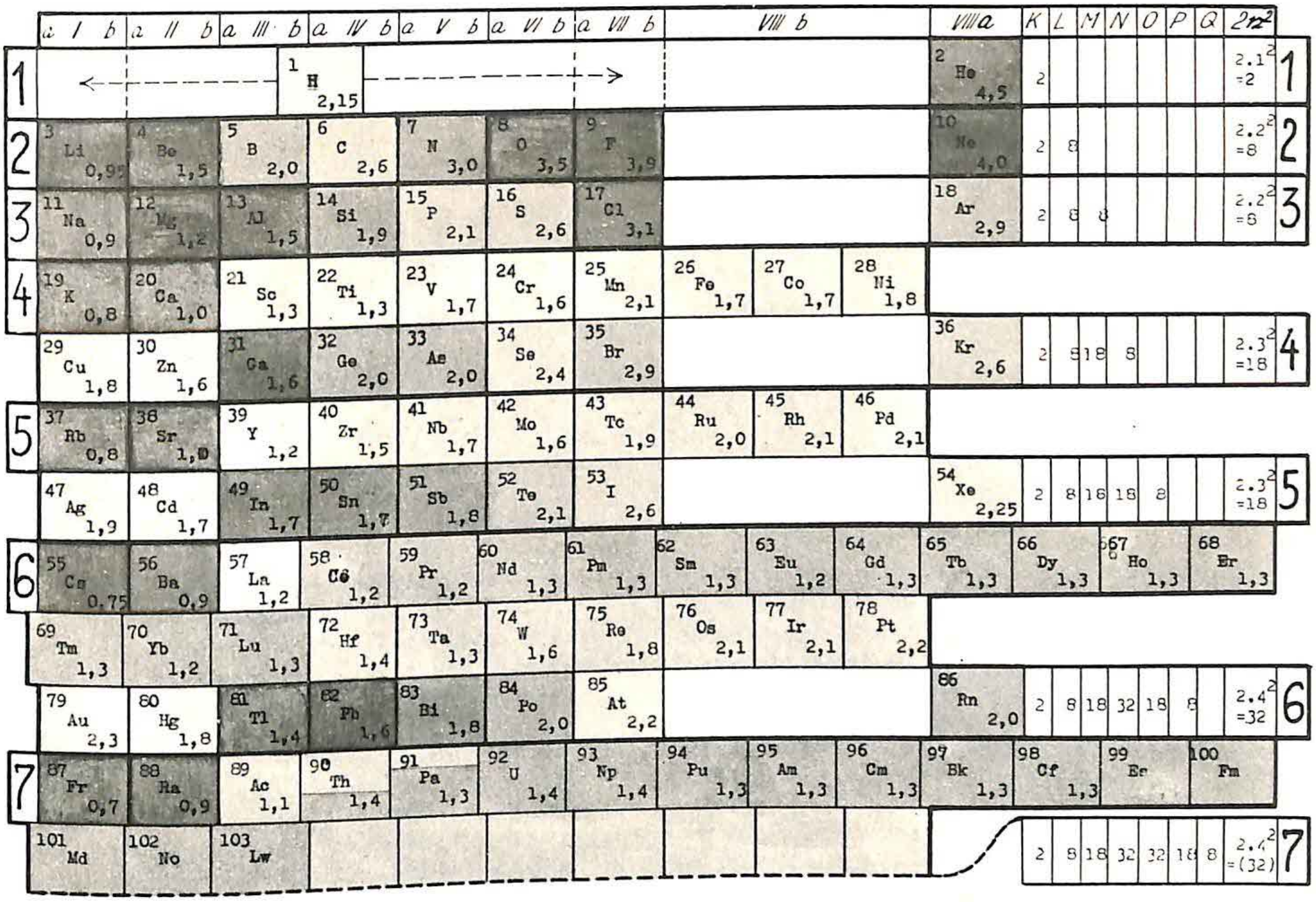


	M1	M2	M2'	M3	M4	M5	M6	M7	M8
1					1 H 2,15				2 He 4,5
2	3 Li 0,95	4 Be 1,5		5 B 2,0	6 C 2,6	7 N 3,0	8 O 3,5	9 F 3,9	10 Ne 4,0
3	11 Na 0,9	12 Mg 1,2		13 Al 1,5	14 Si 1,9	15 P 2,1	16 S 2,6	17 Cl 3,1	18 Ar 2,9
4	19 K 0,8	20 Ca 1,0	30 Zn 1,6	31 Ga 1,6	32 Ge 2,0	33 As 2,0	34 Se 2,4	35 Br 2,9	36 Kr 2,6
5	37 Rb 0,8	38 Sr 1,0	48 Cd 1,7	49 In 1,7	50 Sn 1,7	51 Sb 1,8	52 Te 2,1	53 I 2,6	54 Xe 2,25
6	55 Cs 0,75	56 Ba 0,9	80 Hg 1,8	81 Tl 1,4	82 Pb 1,6	83 Bi 1,8	84 Po 2,0	85 At 2,2	86 Rn 2,0
7	87 Fr 0,7	88 Ra 0,9							

	T3	T3'	T4	T5	T6	T7	T8	T9	T10	T11
4	21 Sc 1,3		22 Ti 1,3	23 V 1,7	24 Cr 1,6	25 Mn 2,1	26 Fe 1,7	27 Co 1,7	28 Ni 1,8	29 Cu 1,8
5	39 Y 1,2		40 Zr 1,5	41 Nb 1,7	42 Mo 1,6	43 Tc 1,9	44 Ru 2,0	45 Rh 2,1	46 Pd 2,1	47 Ag 1,9
6	57 La 1,2	71 Lu 1,3	72 Hf 1,4	73 Ta 1,3	74 W 1,6	75 Re 1,8	76 Os 2,1	77 Ir 2,1	78 Pt 2,2	79 Au 2,3
7	89 Ac 1,1	103 Lw	104							

6	58 Ce 1,2	59 Pr 1,2	60 Nd 1,3	61 Pm 1,3	62 Sm 1,3	63 Eu 1,2	64 Gd 1,3	65 Tb 1,3	66 Dy 1,3	67 Ho 1,3	68 Er 1,3	69 Tm 1,3	70 Yb 1,2
7	90 Th 1,4	91 Pa 1,3	92 U 1,4	93 Np 1,4	94 Pu 1,3	95 Am 1,3	96 Cm 1,3	97 Bk 1,3	98 Cf 1,3	99 Es	100 Fm	101 Md	102 No

Fig.3



	a I b	a II b	a III b	a IV b	a V b	a VI b	a VII b	VIII b			VIII a	K	L	M	N	O	P	Q	2n²	
1	<- - -	- - -	- - -	1 H 2,15	- - -	- - -	- - ->				2 He 4,5	2							2.1² =2	1
2	3 Li 0,95	4 Be 1,5	5 B 2,0	6 C 2,6	7 N 3,0	8 O 3,5	9 F 3,9				10 Ne 4,0	2	8						2.2² =8	2
3	11 Na 0,9	12 Mg 1,2	13 Al 1,5	14 Si 1,9	15 P 2,1	16 S 2,6	17 Cl 3,1				18 Ar 2,9	2	8	8					2.2² =8	3
4	19 K 0,8	20 Ca 1,0	21 Sc 1,3	22 Ti 1,3	23 V 1,7	24 Cr 1,6	25 Mn 2,1	26 Fe 1,7	27 Co 1,7	28 Ni 1,8										
	29 Cu 1,8	30 Zn 1,6	31 Ga 1,6	32 Ge 2,0	33 As 2,0	34 Se 2,4	35 Br 2,9				36 Kr 2,6	2	8	18	8				2.3² =18	4
5	37 Rb 0,8	38 Sr 1,0	39 Y 1,2	40 Zr 1,5	41 Nb 1,7	42 Mo 1,6	43 Tc 1,9	44 Ru 2,0	45 Rh 2,1	46 Pd 2,1										
	47 Ag 1,9	48 Cd 1,7	49 In 1,7	50 Sn 1,7	51 Sb 1,8	52 Te 2,1	53 I 2,6				54 Xe 2,25	2	8	18	18	8			2.3² =18	5
6	55 Cs 0,75	56 Ba 0,9	57 La 1,2	58 Ce 1,2	59 Pr 1,2	60 Nd 1,3	61 Pm 1,3	62 Sm 1,3	63 Eu 1,2	64 Gd 1,3	65 Tb 1,3	66 Dy 1,3	67 Ho 1,3	68 Er 1,3						
	69 Tm 1,3	70 Yb 1,2	71 Lu 1,3	72 Hf 1,4	73 Ta 1,3	74 W 1,6	75 Re 1,8	76 Os 2,1	77 Ir 2,1	78 Pt 2,2										
	79 Au 2,3	80 Hg 1,8	81 Tl 1,4	82 Pb 1,6	83 Bi 1,8	84 Po 2,0	85 At 2,2				86 Rn 2,0	2	8	18	32	18	8		2.4² =32	6
7	87 Fr 0,7	88 Ra 0,9	89 Ac 1,1	90 Th 1,4	91 Pa 1,3	92 U 1,4	93 Np 1,4	94 Pu 1,3	95 Am 1,3	96 Cm 1,3	97 Bk 1,3	98 Cf 1,3	99 Es	100 Fm						
	101 Md	102 No	103 Lw									2	8	18	32	32	18	8	2.4² =(32)	7

Fig 4

Section 2 Molecular structure

During the past ten years, colleges and universities all over the world have been introducing courses on valency and molecular structure. These cover material which is fundamental to all branches of chemistry and can conveniently precede separate courses in inorganic, organic or physical chemistry. The syllabus described by A. K. Colter is typical of many, and the list of experiments for laboratory work to supplement the lectures should be helpful to those engaged in starting up similar courses.

One of the outstanding achievements of the quantum mechanical treatment of molecular structure has been the insight it gives to the behaviour of benzenoid systems. D. P. Craig's article deals with the importance of the "aromatic sextet" of electrons, and why this sextet is so stable. He discusses the physical properties that are in some degree characteristic of aromatic molecules, and shows how this leads to a more general extension of the term "aromaticity".

For an account of molecular-orbital theory applied to transition metal complexes, see the article by H. B. Gray in *Journal of Chemical Education*, 1964, p. 2.

A very useful survey of experimental methods, for the determination of molecular structure, by R. S. Nyholm, will be found in Chapter 7 of the OECD publication *Chemistry To-day*.

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A Sophomore-level Course in Valence and Molecular Structure

In 1959 a complete reexamination of the undergraduate chemistry program was undertaken by the faculty of the Department of Chemistry at Carnegie Institute of Technology. The study led to extensive changes, beginning in the fall of 1960 and now essentially complete.. The most distinguishing feature of the revised curriculum is a course entitled "Valency and Structure," taken in the fall semester of the sophomore year by all students majoring in chemistry and chemical engineering. The course was taught for the fourth time during the fall of 1963 and has now been developed to the stage where further changes in subject matter and adjustments in depth of presentation are expected to be minor.

This paper will consider these points: the general philosophy and objectives leading to the new course, the organization of the course and the course content, and the revised curriculum as a whole, especially with respect to the impact of the Valency and Structure course.

General Philosophy and Objectives

In considering weaknesses in our old curriculum, one fact stood out: many of our most capable students were losing interest during the sophomore year and were frequently changing major fields. The only chemistry courses offered to sophomores at that time were courses in qualitative and quantitative analysis. While it was recognized that these courses performed very necessary functions, it was felt that neither qualitative nor quantitative analysis, at least as they were then being taught, was ideally suited for the course following freshman chemistry.

Some of the objectives of the course following freshman chemistry are the following:

It should complement the freshman course. One of the most significant changes in the undergraduate curriculum during the past decade has been the transformation of the freshman course from a course which is mainly descriptive inorganic chemistry to a course in chemical principles. The change has been a necessary one; however, the student's view of chemistry at the end of the freshman year is becoming increasingly abstract every year. Few would dispute the fact that today's student knows much less descriptive chemistry at the end of his freshman year than the corresponding student 10 to 20 years ago. Nevertheless, an important part of chemistry, now as before, is concerned with the synthesis of new compounds and examination of their properties. It was felt that some changes in the student's view of chemistry are needed at this point.

It should make contact with the frontiers of chemistry, create a sense of participation in the science, and generate student interest. One of the key ideas to get across in any course in chemistry, no matter how elementary, is that chemistry is exploration and adventure. Controversy and uncertainty exist almost everywhere and ideas which are accepted today will be discarded before the student graduates. Any course in chemistry, regardless of level, which does not maintain some contact with the frontiers, which does not point out controversies, which does not continually caution that the available evidence for a given theory is not entirely conclusive, which does not suggest the need for specific experiments which the student can appreciate, misrepresents the science of chemistry and fails to sell it in the most exciting way. We have found that a course in molecular structure lends itself ideally to the presentation at an elementary level of many of the newest and most exciting developments.

It must fulfill certain practical requirements. In view of the ever-increasing amount of essential information to cover in the undergraduate program in chemistry, the luxury of requiring a course which does not cover its share of the basic material cannot be afforded. Much of the subject matter covered in the Valency and Structure course is commonly covered during the early weeks of the typical beginning organic course and later repeated during the early weeks in the first inorganic course. Most of the remainder is traditionally covered in physical chemistry and in the more advanced organic and inorganic courses. It is felt, therefore, that the course is not a "luxury," since it covers almost entirely material now considered an essential part of a good undergraduate training; in fact, by combining material basic to both the organic and inorganic courses, considerable needless repetition is avoided.

Laboratory work in the sophomore year should continue the student's training in the essentials of experimental chemistry as well as teach principles. In achieving these objectives it is held that, all other things equal, an experiment utilizing techniques representative of modern experimental chemistry is to be preferred over one using obsolete procedures.

The Course Organization and Content

The time allotted to the course is 3 hours per week of lectures and an average of 3 hours per week of laboratory

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work, for 15 weeks. The laboratory is required for chemistry majors only. Of approximately 42 lectures, the first 22 are given by an inorganic chemist and the last 20 by an organic chemist. An integral part of both parts of the course is weekly problem assignments based on the lectures and the reading. The subject matter covered in the inorganic portion of the course is outlined in Table 1.

Table 1. Topics in the Valency and Structure Course

	Inorganic
1–4	Structure of the Atom: The nucleus, atomic spectra, the Bohr atom, wave mechanics, the Schrödinger equation
5–11	The Covalent Bond: Ionic bonds, covalent bonds, Lewis formulas, formal charge, molecular orbital and valence bond methods, bond hybridization, resonance, types of hybridization, and geometries
12, 13	Bond Energies, Electronegativities, Bond Lengths: Bond energies and their determination, Pauling and Mulliken electronegativity scales, ionic character, bond moments, bond lengths, covalent radii, bond length as a function of bond polarity
14, 15	Periodicity of the Elements: Description of periodic table, inert gases, metallic character, ionization potentials, atomic and ionic radii, stabilities of oxidation states
16–18	Modern Aids in Structural Studies: Magnetic susceptibilities, dipole moments, molecular spectra
19–21	Complexes and Inorganic Stereochemistry: Chelates and factors determining their stabilities, inorganic isomerism, stereoisomerism of inorganic complexes, crystal field theory
22	Inorganic Nomenclature
	Organic
23–34	Structures of Organic Molecules: The aliphatic hydrocarbons: structure, bonding, geometry, bond lengths, bond strengths, restricted rotation, non-bonded interactions, and conformations in acyclic systems Isomerism in aliphatic hydrocarbons Cyclic systems: strain theory, geometrical isomerism, conformational analysis Benzenoid aromatic compounds Functional groups: organic nomenclature, stereoisomerism, and optical activity Chemical topology, tautomerism
35–37	Physical Properties of Organic Compounds: Intermolecular forces: ion-dipole forces and solvation, dipole-dipole forces, polarizability, hydrogen bonding Intermolecular forces and physical properties: melting point, boiling point, solubility, refractive index
38–41	Generalized Acid-Base Behavior and Addition Compounds: General concepts, definitions, organic acids and bases, structural effects on acidity and basicity Onium salts, carbonium salts, charge-transfer complexes, sandwich compounds (the metallocenes), inclusion compounds
42	Further Applications of the Theory of Resonance: Nonbenzenoid aromatics, heterocyclic compounds, Hückel 4n + 2 rule

Essentially all of the subject matter covered in the first 22 lectures is traditionally covered in a junior or senior course in inorganic chemistry. The depth of presentation must be adjusted to some extent but not enough to appreciably weaken the presentation. Concurrently with the Valency and Structure course the student is taking his third semester of calculus and his third semester of physics. The first two semesters of physics cover mechanics, heat and thermodynamics, and mechanical waves. The text presently used for the first half of the course is "Inorganic Reactions and Structure" by E. S. Gould. The material covered roughly corresponds to that in Chapters 1 ("Structure of the Atom; Atomic Energy Levels"), 3 ("The Covalent Bond"), 7 ("Trends Within the Periodic Table; The Rare Gases"), 9 ("Bond Energies, Electronegativities, and Covalent Bond Lengths"), 18 ("Inorganic Nomenclature") 22 ("Complexes and Inorganic Stereochemistry") and 25 ("Magnetic Susceptibility, Dipole Moments, and Molecular Spectra as Aids in Structural Studies"). Some of the assigned problems have been taken from the text in the past and it has been our experience that these are of about the correct difficulty.

Approximately the first half of the inorganic portion of the course will be recognized as being largely an extension of topics covered in the modern freshman course. These subjects are covered in much greater depth and in much more quantitative terms in Valency and Structure, however. As an example, the student at this stage has some appreciation of what a differential equation is and can understand, at least qualitatively, how the quantum numbers arise from solution of the Schrödinger equation. Further, the demands on the student in terms of his level of understanding and ability to make use of the concepts relating to atomic structure and covalent bonding are much more severe than in freshman chemistry.

The emphasis in the second half of the inorganic portion of the course is on structures and geometries of inorganic molecules, properties of inorganic compounds as a function of structure, and methods used to determine structure. This portion of the course is more descriptive but still places heavy stress on underlying principles.

The subject matter covered in the organic portion of the course (Table 1) is organized according to the different kinds of forces involved: first, forces between atoms (structures of molecules); next, "physical" or weak intermolecular interactions (physical properties); and finally, the most general kind of stronger or "chemical" interaction between molecules, namely, generalized acid-base or electron donor-acceptor interaction.

The material covered in the organic half makes repeated and extensive use of many of the concepts developed in the first half. A partial list of such concepts includes bond hybridization, electronegativities, bond polarities, bond energies, bond lengths, resonance, molecular orbital and valence bond theories, and physical methods of structure determination. Most of the material covered in the second half of Valency and Structure is traditionally covered in beginning and advanced organic chemistry. The presentation here is far from a traditional introduction to organic chemistry, however. The text for this part of the course was written by the author and is supplied to the students through the school bookstore for cost. Additional reading from organic texts and THIS JOURNAL is suggested and assigned.

Beginning with bonding and geometry in the simplest aliphatic hydrocarbons methane, ethylene, and acetylene, we next proceed to discuss nonbonded interactions in ethane and restricted rotation about carbon-carbon single bonds in acyclic systems. Some facility in writing structural formulas is gained in considering skeletal, positional, and geometrical (cis-trans) isomerism in aliphatic hydrocarbons. Proceeding next to cyclic systems, the discussion covers ring strain, geometrical isomerism, and again, restricted rotation about carbon-carbon single bonds. The ideas introduced in discussing restricted rotation are then extended to an introduction to conformational analysis in cyclohexane and derivatives of cyclohexane.

The section on benzenoid aromatic hydrocarbons starts with a consideration of bonding and geometry. The structure of benzene is described in both valence bond and molecular orbital language. The concept of resonance energy is examined carefully and critically. With polynuclear aromatic hydrocarbons, the use of Kekulé structures to define bond orders which can be used to predict bond lengths is discussed.

The section on functional groups is introduced with the proposition that the fundamental problem of organic chemistry is to correlate properties with structure; that is, given the structure of an organic molecule, to predict the compound's properties, or vice versa. Taking as diverse examples of properties the analgesic potency of compounds related to the opium alkaloids, color, tensile strength, and reactivity in a chemical reaction, it is instructive to show, using real examples, how the present experimental attack on the "fundamental problem" may vary from one which is essentially trial and error to one in which quantitative correlations already lead to fairly reliable predictions. We then note that the classification of compounds by homologous series according to functional group is one of the oldest and most useful correlations of structure and properties.

After discussing bonding and geometry in the simpler members of the principal homologous series we next diverge to consider some of the methods used by the organic chemist to determine the structure of an uncharacterized organic compound. The discussion covers these topics: determination of the molecular formula and preliminary information from the molecular formula, classification tests for functional groups, synthesis, degradation, physical methods, and use of isomer number. The methods are illustrated with simple examples and by assigned problems.

The section on Structures of Organic Molecules is completed with a fairly thorough coverage of organic nomenclature and stereoisomerism and briefer discussions of chemical topology and tautomerism.

After covering chemical bonding and interactions within molecules we turn to interactions between molecules. Here the different kinds of weaker or so-called physical intermolecular interactions are first discussed as a function of structure. After considering the ways the common physical properties such as melting point, boiling point, and solubility depend on these interactions, an attempt is made to correlate these properties with structure.

We next turn to the most general kind of stronger or so-called chemical interaction between molecules, namely, generalized acid-base or donor-acceptor interaction. The discussion first covers generalized acid-base behavior, acid-base properties of organic compounds, and acid-base properties as a function of structure. We then look at several different classes of compounds loosely termed addition compounds, most of which are formed, at least formally, through acid-base interaction in the generalized sense.

An important feature of the presentation of the organic material is a heavy emphasis on energetics. Besides the consideration of bond energies, energy relationships are an important part of the discussions of restricted rotation, geometrical isomerism, ring strain, conformational analysis in cyclic systems, resonance, tautomerism, and intermolecular forces. Discussion of the effect of structure on transition temperatures is usefully centered around the enthalpy and entropy of transition. For a reversible phase transition at constant T and P

$$\Delta H = T\Delta S(\Delta F = 0), \quad T = \Delta H/\Delta S$$

The effect of molecular rigidity is reflected in ΔS and the effect of intermolecular forces (function of molecular shape and functional groups) in ΔH. For fusion, both ΔH and ΔS vary widely, with changes in ΔS frequently dominating (e.g., compare *n*-pentane, isopentane, and neopentane). For vaporization, changes in ΔS are much smaller (Trouton's rule) and boiling points depend mostly on the magnitude of the intermolecular forces. The students at this point have had previous exposure to the concepts of free energy and entropy in both freshman chemistry and freshman physics.

The valency and structure laboratory is a sharp departure from the traditional sophomore laboratory. With the exception of experiment 7, it complements the first half of the course. The main emphasis is on the experimental techniques used by the modern inorganic chemist in making new compounds and in determining their structure. No laboratory text is used; instead, a mimeographed set of very general instructions including a limited amount of background information and references for further reading was prepared by two of the faculty. A class of 20 to 25 chemistry majors is divided into 2 sections. An average of about 6 hrs per experiment is allotted, with some experiments easily completed in a single 3-hour period and others requiring up to 3 laboratory periods.

The experiments used last year are listed and briefly described in Table 2. All experiments were not equally successful and a few additional changes in the laboratory are likely to be made during the next two or three years.

Table 2. Valency and Structure Laboratory

1. Preparation of Aluminum(III) Iodide (sealed tube reaction, sublimation, molecular weight determination)
2. (*a*) Operation of the Spectrophotometer; (*b*) Spectrophotometric Determination of the Formula of a Complex Ion (copper-iminodiacetic acid complex, Beckmann Model DU Spectrophotometer); (*c*) Determination of the Visible Spectra of cis and trans Isomers of Coordination Compounds (*cis*- and *trans*-[Co(ethylenediamine)$_2$Cl$_2$]Cl)
3. Preparation of Sodium Amide (use of inert atmosphere dry box)
4. Glass Blowing (pyrex, oxygen torch)
5. Preparation of Copper(I) Chloride
6. Vacuum Manipulation of Volatile Compounds (vapor pressure measurements on CCl_4 at a series of temperatures using a vacuum assembly)
7. The Leveling Effect of Solvents and the Determination of the Relative Strengths of a Series of Acids in Glacial Acetic Acid (potentiometric titrations)
8. Properties of cis and trans Isomers of Coordination Compounds (preparation of *cis*- and *trans*-[Co(ethylenediamine)$_2$Cl$_2$]Cl, resolution of the cis isomer, measurement of magnetic susceptibilities, infrared spectra, and dipole moments)

The Revised Curriculum

Although the Valency and Structure course has had some impact on the teaching of all other chemistry courses following it, the beginning organic course and the senior inorganic course have felt the greatest influence. The organic course starts immediately with organic reactions and essentially no time need be devoted to structure and nomenclature. A complete discussion of each reaction, including stereochemical aspects, can now be given from the very beginning. As an example, a discussion of bromine addition to olefins during one of the early lectures could include addition to cyclohexene to give *trans*-1,2-dibromocyclohexane and addition to *cis*- and *trans*-2-butene to give *dl*- and *meso*-2,3-dibromobutane, respectively.

The sequence of chemistry courses in the new curriculum is shown in Table 3. An important feature of the revised curriculum is the flexibility offered in the senior year. Nearly all of the required chemistry courses have been completed by the end of the junior year, leaving room for 55 units ($18^1/_3$ semester hours) of technical electives in the senior year. The needs of the student planning to take a job after earning the BS degree are quite different from those of a student planning graduate work in chemistry. For the latter group two-semester basic graduate courses in the three areas, physical, organic, and inorganic-nuclear chemistry are available. Our better students commonly take one or two of these basic graduate courses during their senior year and one student has taken all three. The basic graduate course in inorganic-nuclear chemistry can be substituted for the regular senior course. The jump to the graduate course is made easier for the undergraduate student by the background in modern inorganic chemistry gained from the Valency and Structure course.

Table 3. Sequence of Chemistry Courses in the Revised Curriculum

Semester	Course		
1	. . .	General Chemistry	. . .
2	. . .	General Chemistry	. . .
3	. . .	Valency and Structure	. . .
4	. . .	Physical Chemistry I	Chemical Measurements I
5	Organic Chemistry I	Physical Chemistry II	Chemical Measurements II
6	Organic Chemistry II	Physical Chemistry III	. . .
7	Qualitative Organic Analysis	. . .	Inorganic and Nuclear Chemistry
8	. . .		Instrumental Analysis

Conclusions

The Valency and Structure course has been enthusiastically received by the students. The level of student interest and participation in the courses in organic and physical chemistry which follow is now noticeably higher. The course has been a popular elective for sophomores from other departments who (usually by reason of advanced standing in one or more subjects) have sufficient flexibility in their course program. In each of the three years the course has been taught, it has influenced one or more outstanding students from other departments to become chemistry majors. The loss of capable chemistry majors during the sophomore year has stopped. Finally, the course provides the necessary foundation for a truly modern beginning organic course.

The author gratefully acknowledges important contributions to the development of the Valency and Structure course by Professors Robert R. Holmes, Albert A. Caretto, and Walter A. Manch.

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THE CHANGING CONCEPT OF AROMATIC CHARACTER

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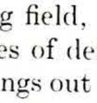
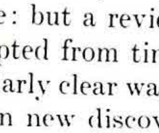
What do we mean by saying that a molecule has 'aromatic character'? Can a molecule have aromatic character and yet not be an aromatic molecule?

The current state of knowledge, and especially recent developments both in the synthesis of new types of molecule, and in theoretical understanding, promote these questions to matters of some substance. The search for a definition of what constitutes aromatic character is, as in any rapidly changing field, a sterile one: but a review of the types of definition adopted from time to time brings out in a particularly clear way the intimate connexion between new discoveries and the progressive development of interpretative concepts. The now extensive literature will indeed show that while the definition of an aromatic molecule has given little trouble, 'aromatic character' has been, and still is, a vague term with a meaning that has changed with advancing factual and theoretical knowledge. This article is devoted to the present state of the subject and to some developments in view.

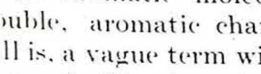
The class of aromatic molecules has long been taken to include benzene and its homologues with benzenoid ring systems, beginning with naphthalene, anthracene and phenanthrene, and their derivatives:



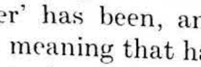
Benzene



Naphthalene



Anthracene



Phenanthrene

The chemical characteristics of aromatic molecules were largely known many years ago, and those characteristics that could be said to be common and peculiar to aromatics together constituted the then current idea of aromatic character. They included chemical inertness compared with open-chain conjugated molecules such as butadiene, as in their inertness to addition reaction with bromine. There was also the fact that when an aromatic molecule reacts it very often does so with preservation of the aromatic nucleus, as in the reaction of benzene with nitrating agents to give nitrobenzene.

ELECTRONIC THEORIES

By the 1920s the chemical properties of aromatics were being interpreted by Ingold and by Robinson as consequences of the electronic make-up of the molecules and of the electronic transitions determining the course of chemical reactions. The lack of reactivity of benzenoid systems, for example, was rationalized in the proposal that a benzene ring has a set of six electrons, called the *aromatic sextet*, which is highly stable and resistant to disruption by chemical attack. In later more explicit versions of this theory the six electrons are called π-electrons: each carbon atom provides one such electron, and in the free carbon atom the electron is in a $2p_\pi$ atomic orbital of the kind shown in the upper diagram of Fig. 1.

When the carbons are joined together in a molecule of benzene the six electrons are no longer localized on the atomic centres, but *delocalized* over the molecular framework, as shown in the lower diagram.

The aromatic sextet is the analogue of the atomic octet, in the sense that it is a group of electrons making a molecular closed-shell just as the eight electrons of the octet make an atomic closed shell. The reason why the stable grouping of electrons in the molecule is six was not given until later, and to explain its physical basis we must consider the molecular-orbital description as first given by Hückel; however, recognition of the aromatic sextet as an empirical feature of stable systems is itself of great value. It at once gives a basis to understand the fact that in the five-carbon system it is the negative ion with six π-electrons that is of special stability, whereas in the seven-carbon tropylium system it is the positive ion:

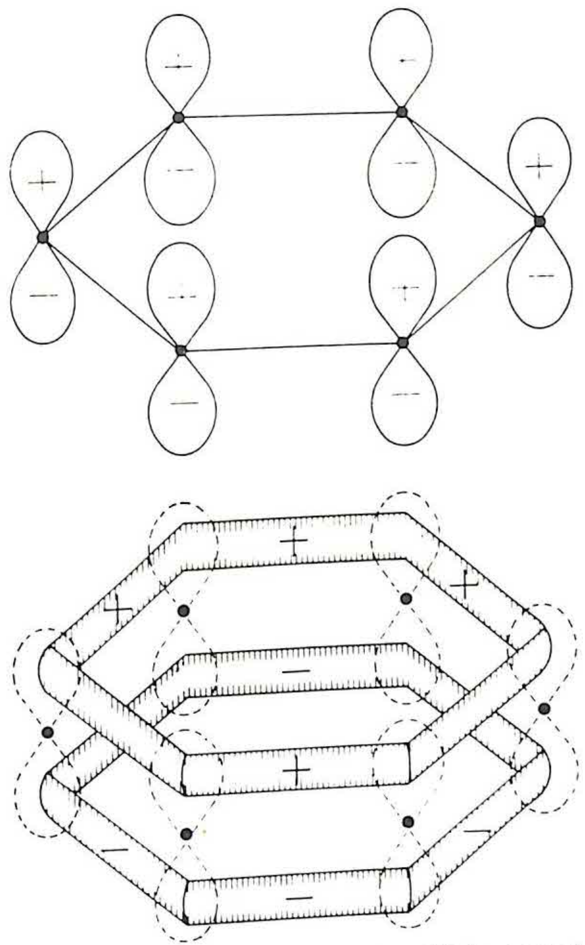
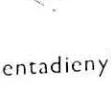
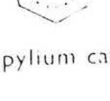


Fig. 1. The carbon $2p\pi$ atomic orbitals (upper) and delocalized molecular orbital (lower). (After Coulson, *Valence*, Oxford University Press, 1961, p. 240).



Cyclopentadienyl anion



Tropylium cation

THE MOLECULAR-ORBITAL DESCRIPTION

The lower diagram of Fig. 1 illustrates the electronic situation in which electrons are delocalized over all six carbon centres of a benzene ring, giving a smeared-out charge distribution, corresponding to the overlapping and merging of the individual atomic electron clouds. According to wave-mechanical theory, electrons spreading over a number of centres in this way are more stable, because their kinetic energy, which decreases with increasing wavelength, is less and the binding energy greater. In the molecular-orbital theory this principle is given semi-quantitative expression. We find functions called molecular orbitals (m.o's) with properties allowing them to play a part in molecules similar to that of atomic orbitals in atoms, by describing how the electrons will move and be distributed under the influence of all the forces present, namely the attractive forces between the electrons and the nuclei, and the repulsive forces between different electrons.

Thus the essential idea of a molecular orbital is that it describes an electron spreading over two or more atomic centres, instead of being confined to one, as in an atomic orbital (Fig. 1). The Pauli exclusion principle applies to molecular orbitals as it does to atoms to require that no more than two electrons with opposite spins can occupy one molecular orbital: of the six π-electrons in benzene two go into the molecular orbital depicted in Fig. 1. This is the most stable orbital, because it has no nodal plane perpendicular to the plane of the molecule—a condition that gives the longest possible electron wavelength and the greatest binding energy. The next most stable orbitals are those with a single nodal plane, shown in projection on to the molecular plane in Fig. 2. The high symmetry of the benzene system is associated with a *degeneracy* of these two orbitals, and their energies are equal. The nodal planes must be at right angles to one another, but may otherwise be placed without restriction. Four electrons fully occupy these two molecular orbitals and, together with the two in the most stable orbital, account for the six π-electrons. There are still other molecular orbitals of benzene, not occupied in the ground state. The energies of the orbitals may be calculated and are included in the complete set of m.o. energy levels shown in Fig. 3. We can now understand why a sextet of electrons is so stable. If the orbitals shown were occupied only by five electrons there would be an electron vacancy in the molecule that would give it an electron-attracting character and so make it chemically reactive. If the molecule had seven electrons, one would have to occupy a higher energy orbital and would be readily lost, again giving chemical reactivity.

The molecular-orbital viewpoint allows some other experimental facts to be fitted into a simple pattern. We expect a sextet to be stable whenever the sequence of a single level followed by two degenerate levels is followed, and it is so even in regular plane five- and seven-membered rings, such as those of the cyclopentadienyl and tropylium systems already referred to. In the five-membered ring system the sextet is attained in the *anion*, and in the seven-membered system in the *cation*, and the expected stability is indeed found in the ions and not in the neutral molecules.

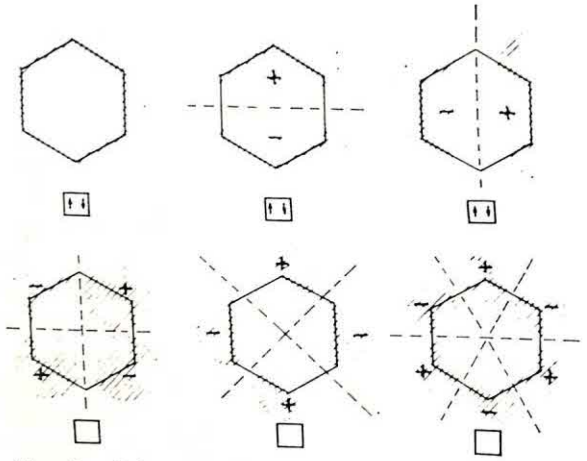


Fig. 2. Schematic diagram of the molecular orbitals of benzene, showing (first row) the nodeless most stable orbital, the less stable degenerate pair and (second row) the excited orbitals unoccupied in the ground state. (After Seel, *Atomic Structure and Chemical Bonding*, Methuen, 1963, p. 51).

No special stability is associated with the aromatic octet, found in the molecule cyclo-octatetraene shown, with its molecular-orbital energy diagram, in Figure 4. Two electrons occupy the most stable m.o., four more occupy the degenerate pair of higher energy, and the remaining two are left to half-fill degenerate orbitals, which are not stabilized relative to atomic orbitals. The averaged stabilization taken over all the electrons is much less than in benzene. Since the planar configuration of an eight-membered ring system can only be held at the cost of strain energy in the single bonds, and because the possible energy gain from the free spreading of the electrons over the planar configuration is so slight, the molecule adopts a non-planar boat structure shown in Fig. 5, in which adjacent atomic orbitals can overlap only by pairs, giving a polyolefinic electronic character with alternate double bonds (1·34Å) and single bonds (1·46Å).

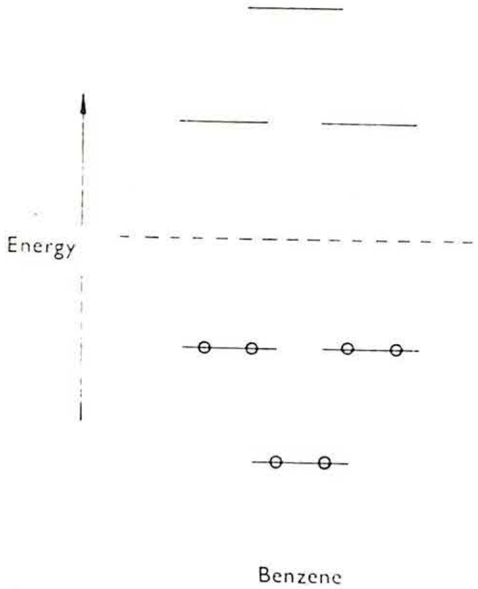


Fig. 3. The one-electron orbital energies of benzene. In the ground state the lowest three orbitals are each doubly occupied by electrons.

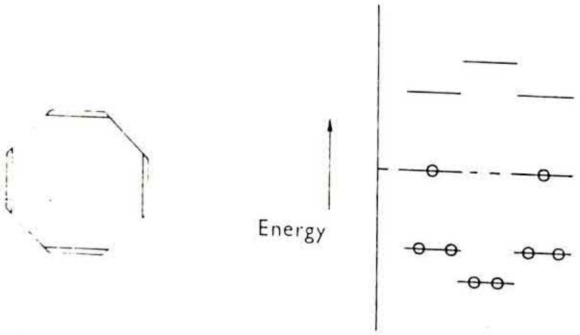


Fig. 4. Cyclo-octatetraene (*left*) and its one-electron orbital energies (*right*). In the ground state the lower three orbitals are doubly filled, and the next two orbitals half-filled.

The general proposition that cyclic unsaturated molecules have aromatic character only when no m.o's are part-occupied is known as *Hückel's rule*. It can be expressed in the statement that systems of $(4n + 2)$ π-electrons are aromatic, and systems of $4n$ are not. Apart from benzene and the non-planar molecule of cyclo-octatetraene no monocyclic molecules with alternating double and single bonds have been known until the last three or four years, during which Sondheimer and colleagues have prepared the large-ring fully conjugated 'annulenes' $C_{14}H_{14}$, $C_{18}H_{18}$, $C_{20}H_{20}$, $C_{24}H_{24}$, and $C_{30}H_{30}$, three of which are $(4n + 2)$ molecules and two (the third and fourth) are $4n$ molecules. The first compound, [14]-annulene has a carbon skeleton like the peripheral atoms of the benzenoid molecule pyrene:

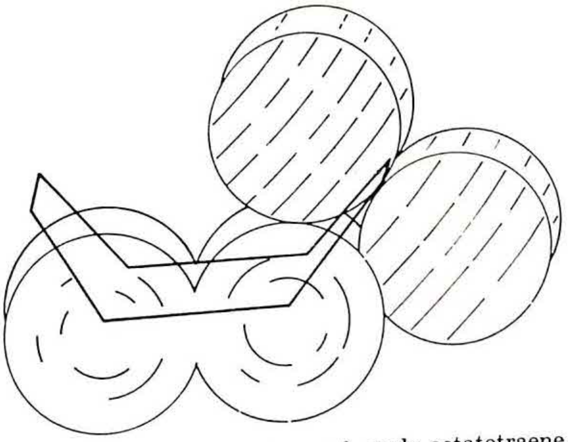
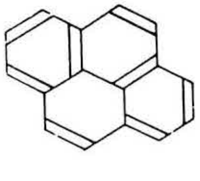
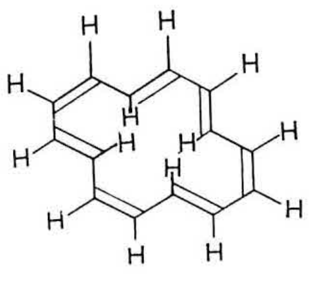


Fig. 5. The tub structure of cyclo-octatetraene, showing the pair-wise overlapping of π-orbitals. Because adjacent pairs do not overlap there is no cyclic delocalization.



Pyrene



[14]-Annulene

Ten of the hydrogen atoms lie outside the skeleton and four lie inside. This molecule, although one of the Hückel $(4n + 2)$ class, does not show aromatic properties. On the other hand [18]-annulene, which is perhaps the most studied example so far, is a planar molecule and has the magnetic properties required for aromatic character. Again [24]-annulene is not aromatic.

THERMOCHEMICAL AND MAGNETIC PROPERTIES

The arguments that we have just reviewed draw attention to the origin of the special stability of aromatic molecules in their electronic structure, and in particular to the delocalization of the aromatic π-electrons. It is a natural next step to inquire what physical properties such electrons possess, and to deal with physical criteria of aromatic character. If such criteria could be set, they would allow delocalized electrons to be proved in non-aromatic molecules, such as heterocyclics, and so lead to a generalization extending aromatic character into a much wider class of molecules. We shall refer to two such physical properties, both of which have been exploited in this way.

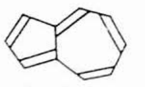
When aliphatic hydrocarbons are burned their heats of combustion may be represented as sums of parts belonging to individual C–C and C–H bonds, and, once a set of bond heats has been found from a number of reference compounds, heats of combustion of other molecules may be predicted fairly reliably. The same may be done for olefins, in which the carbon–carbon double bonds make a contribution to the heats of combustion greater than for single bonds but the same in different olefins. Now benzene is formally held together by alternating double and single bonds, and a heat of combustion may be calculated for it as if it were a cyclic polyolefin. This calculated value exceeds the measured heat of combustion by 36 kcal mole^{-1}, showing that benzene is more stable by this quantity than would be expected if its bonds were strictly either pure double or pure single bonds. This stabilization is the measure of the energy gain from the delocalization of the π-electrons, and is the *resonance energy* or *delocalization energy*. Representative values are shown in Table I.

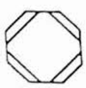
TABLE I

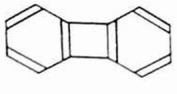
RESONANCE ENERGIES OF BENZENOID AROMATICS
(kcal mole⁻¹)

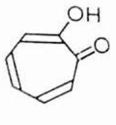
Molecule	Resonance Energy	Resonance Energy per π-electron
Benzene	36	6
Naphthalene ..	61	6·1
Anthracene ..	86	6·1
Phenanthrene ..	99	7·1
Diphenyl.. ..	74	6·2
Dibenzyl ..	70	5·8

In these simple aromatic hydrocarbons each π-electron contributes about 6 kcal per mole to the resonance energy. We must now see whether in some selected non-benzenoid molecules the same method gives indications of resonance stabilization. The examples chosen, with the resonance energies found, are given below:


Azulene
31


Cyclo-
octatetraene
4


Diphenylene
20



Tropolone
21

The quantities stated are in kcal mole⁻¹

It is thus confirmed that cyclo-octatetraene in contrast to the other ring systems has no aromatic-type stabilization. None of these is an aromatic compound in the proper sense, but each can be said to have aromatic character according to this physical criterion.

The distinctive magnetic properties show themselves in two different ways. In a magnetic field atomic and molecular electrons are forced to circulate. The charge circulation itself produces a magnetic field in opposition to the applied field and, if there are no other magnetic influences (such as unpaired electron spins), this makes the system display diamagnetism. Electrons that are delocalized over a closed circuit taking in many atomic centres can be induced by the magnetic field to circulate about it, and they make a disproportionately large contribution to the diamagnetism: moreover the contribution is confined to the direction perpendicular to the plane of circulation, namely the molecular plane. Both the mean diamagnetism, and its anisotropy, are measurable quantities and can be used to demonstrate aromatic character. The essential quantitative arguments in this case, as in that of resonance energy, depend on the exaltation of the diamagnetic susceptibility of a delocalized system above the sum of contributions by the parts, in this case individual atoms. The atomic contributions are Pascal's diamagnetic constants: in molecules without delocalized electrons the molecular diamagnetism is quite well given by the Pascal sum, but we see from the values collected in Table II that aromatic molecules are all exalted. Cyclo-octatetraene shows no significant exaltation, in harmony with our earlier conclusions, but the aromatic character of azulene and some other molecules lacking a benzenoid skeleton is indicated.

TABLE II

EXALTATION OF DIAMAGNETISM IN HYDROCARBONS
(c.g.s. units)

Molecule	$-10^6\chi$ (exptl)	Pascal sum	Exaltation
Benzene	55·6	36·9	18·7
Naphthalene ..	91·9	55·7	36·2
Chrysene	160·7	93·3	67·4
Azulene	91·0	55·7	35·3
Cyclo-octatetraene	51·9	49·2	2·7
Tropolone	61·0	45·8	15·2
Tropone	54	41·2	12·8

The circulation of π-electrons in a magnetic field has another consequence that can be exploited in measurements of the *proton magnetic resonance*. Let us suppose that the external magnetic field is perpendicular to the plane of the molecule, as shown in Fig. 6. The induced circulation of the π-electrons gives a field which, measured at points within the hexagon, is opposed to the external field. The lines of force of the induced field curl round outside the hexagon, and at the positions of the hydrogen atoms give an increment to the field, making the total field greater than the external field alone. The proton magnetic resonance is a sensitive measure of the total field, and allows an increase to the field of this kind to be detected. Proton magnetic resonance measurements have proved in practice to be useful in identifying molecules with aromatic circulation of electrons. In this way [14]-annulene was shown to be non-aromatic, and [18]-annulene to be aromatic.

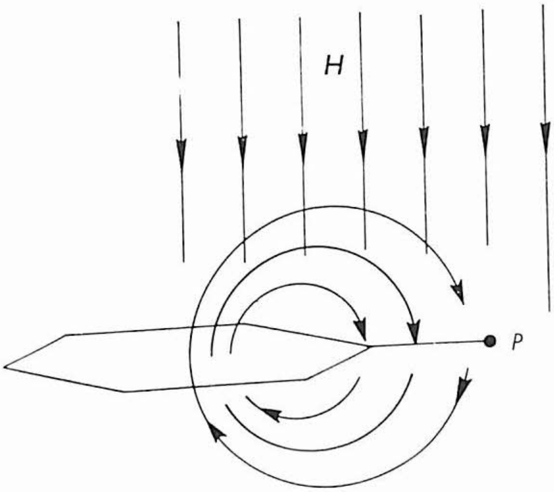
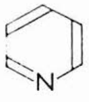


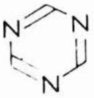
Fig. 6. Schematic diagram of the aromatic ring-current contribution to the magnetic field measured at the hydrogen atoms of benzene. *H* is the external field and the curved lines are lines of force of the induced field of the circulating π-electrons.

THE MORE GENERAL CONCEPT OF AROMATICITY

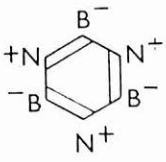
The existence of such distinct physical properties in aromatic molecules, that are in some degree characteristic of them, has been one of the main factors in the generalization of the term aromatic character to molecules beyond the strictly aromatic class. Thus pyridine (I), s-triazine (II), and borazole (III) have aromatic character insofar as they possess the physical properties of delocalized electrons. Atomic theory for nitrogen and boron confirms that both can provide a π-electron to a cyclically delocalized system, and the conditions shown in Figs 1 and 2 can be realized in these cases too. In the special circumstances of borazole the atoms carry net charges B^- and N^+.



I



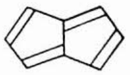
II



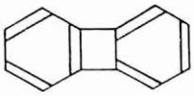
III

THE PSEUDO-AROMATIC MOLECULES

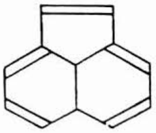
Hückel's rule distinguishes molecules with $(4n + 2)$ π-electrons from those with $4n$, the former being in theory aromatic and the latter not. Since the rule is firmly based only for monocyclic systems its compass is limited, and many interesting cases occur outside the field of its proper application. In practice the $(4n + 2)$ rule seems to apply more widely. For example the bicyclic and polycyclic benzenoid hydrocarbons such as naphthalene, anthracene, phenanthrene and higher homologues have $(4n + 2)$ π-electrons, whereas the unknown bicyclic molecule pentalene, an example of a $4n$ molecule, has resisted preparation by methods which, if pentalene possessed aromatic stability, would have been very likely to succeed. However, in such polycyclic molecules exceptions to Hückel's rule are common. Both biphenylene and acenaphthylene are stable systems with $4n$ π-electrons, twelve in each. One can see that no simple rule that fails to take account of the structure in more detail can be expected to deal correctly with such molecules: it is found for example that the bonds joining the benzene rings in biphenylene are 1·46Å long, so long that the two rings interact only weakly, and we have a molecule owing its stability to a simple duplication of the benzene π-electrons. Nevertheless the search for more general prescriptions to classify polycyclic systems into those with aromatic-type stability and those without is a useful one, and has



Pentalene

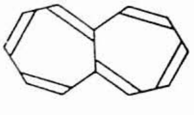


Biphenylene

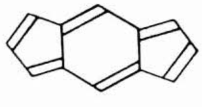


Acenaphthalene

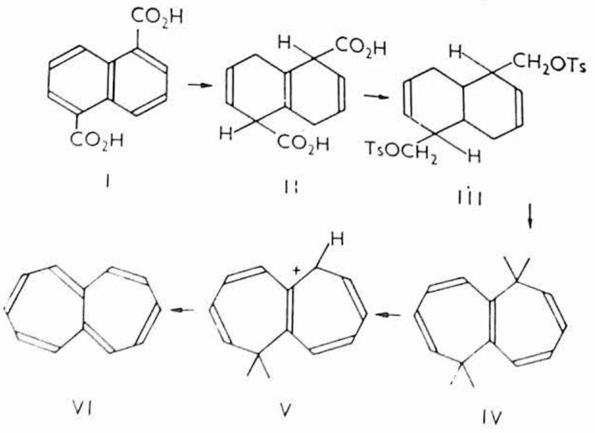
given rise to much theoretical work, and this in turn has stimulated experimental efforts in the synthesis of compounds that seemed to have a special interest. One theoretically based classification depends on the symmetry of the π-electron wave-function of the ground state of the molecule. These monocyclic molecules that are non-aromatic according to Hückel's rule are calculated to have unsymmetrical ground-state wave-functions in the valence-bond approximation, and this unsymmetrical character is closely connected to their lack of stabilization. The hypothesis that an unsymmetrical wave-function is an index of non-aromatic character in all π-electron molecules, polycyclic as well as monocyclic, gives a basis for dividing molecules into aromatic and *pseudo*-aromatic, the latter being expected to lack ordinary aromatic stabilization. Typical *pseudo*-aromatics are pentalene (above) and the molecules of heptalene and benzodipentadiene. Because of the rarity of *pseudo*-aromatics and even of molecules having some resemblance to them, great interest attaches to the recent preparation of heptalene by Dauben and Bertelli. Their method is indicated in the scheme below, beginning with the conversion of naphthalene-1,5-dicarboxylic acid (I) through its ditoluene sulphonate (III) into a mixture of dihydroheptalenes, of which one is shown (IV):



Heptalene



Benzodipentadiene



The dihydroheptalenes were dehydrogenated by use of triphenyl fluoroborate to give the fluoroborate of the heptalenium cation (V) which, on treatment with trimethylamine, gave heptalene. It is a yellow-brown liquid stable only at low temperatures, and rapidly polymerizes in the presence of oxygen or on warming. It is quite clear that this *pseudo*-aromatic molecule reacts in ways suggesting polyolefinic rather than aromatic character. The discovery of this molecule has done much to give substance to the distinction between the *pseudo*-aromatics and others, a distinction that we can express by saying that the fact that a planar molecule with π-bonds can be written in two or more equivalent ways is not a sufficient condition for aromatic stability: other conditions have to be fulfilled as well.

AROMATICITY IN SECOND-ROW RING SYSTEMS

Once aromatic character is divorced from the chemical properties of aromatic molecules, and is held to be an electronic property that can occur in molecules at large, namely that of cyclic electronic delocalization, the field of its possible occurrence is still wider. All the examples we so far have discussed are of molecules formed of elements of the first row of the Periodic Table. Each provides one electron in a $2p_\pi$ atomic orbital and, though the orbitals from different atoms may differ in size and therefore overlapping power, they are of the same symmetry, indicated schematically in the upper part of Fig. 1, and also below in Fig. 7. Second-row elements in their higher valence states are well known to use d-orbitals, some of them being orbitals of π-character, as shown in Fig. 7.

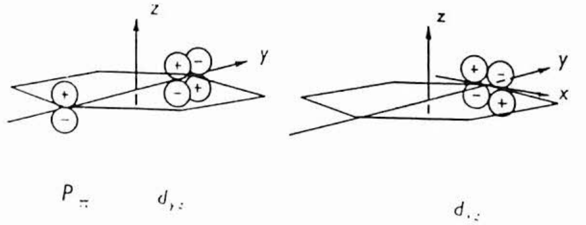
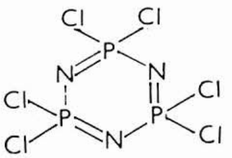
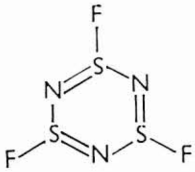


Fig. 7. The two d_π orbitals compared with a p_π orbital. Each d-orbital has four lobes, two above and two below the molecular plane.

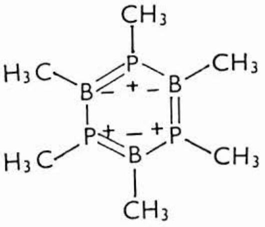
The term 'π-character' means that, under reflection in the molecular plane, the orbital wave-function changes its sign, the positive regions in Fig. 7 being mapped on to the negative regions and *vice versa*. Among the d-orbitals there are two that have this property: both are capable of overlapping with similar orbitals on adjacent atoms, or with p_π orbitals on adjacent atoms, in ways that could lead to delocalization. In fact ring systems made by second-row elements alone are uncommon (an example is the -Si-S-Si- system) but ring systems with alternating first-row and second-row elements are quite well known. Some examples are shown:



Phosphonitrilic chloride



Thiazyl fluoride



Methyl phosphoborine

We can study the delocalization properties of these ring systems by molecular-orbital theory, allowing for the differences between p- and d-orbitals. Each first-row element provides one electron in a p_π orbital, as usual, and each second-row element provides an electron in a d_π orbital. In phosphorus, for example, as in the phosphonitrilic halides, it is very reasonable that it should do so. X-ray studies show that the atoms about each phosphorus are arranged approximately tetrahedrally, so that the s- and p-orbitals of phosphorus's valence configuration, sp^3d, are used in forming single bonds to give the skeletal framework of the molecule. The remaining electron is a d-electron, and that one we suppose to take part in the delocalized system. The proof that these more complex systems do indeed display properties expected of delocalized systems is far more difficult an experimental matter, because we do not have reference compounds with which to compare, for example, their thermochemical and magnetic properties. However, some theoretical progress has been made in exploring possible differences between this class of potential delocalized systems and more familiar ones. Some of these are interesting and suggestive of lines of experimental research: there is for example the finding that systems of alternating first-row and second-row elements do not follow Hückel's rule of alternating aromatic and non-aromatic systems with increasing ring size. In fact phosphonitrilic compounds are known with rings of 6, 8, 10, . . . 20 members, and no alternation of properties is found. However, this is a new field of research in which much has still to be done before theory and practice can be put side by side; it is already clear that progress can be made, and it seems likely that a completely new type of aromaticity will be recognized as the result of it. We shall then have the position that aromatic character is of at least two fundamentally distinct types, of which only one has been seen in the delocalized systems of first-row elements, the other being of even wider occurrence in systems where d-electrons play a part in valence phenomena. This is known to be the case in second-row elements and in transition metals, and must certainly be far more widespread even than that.

REFERENCES

A fuller discussion of this subject, with the key references, is given in an article by the writer in *Non-Benzenoid Aromatic Compounds*, Ed. D. Ginsburg, Interscience, 1959, 1.

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Gaoni and Sondheimer, *J. Amer. chem. Soc.*, 1962, **84**, 3520, and references therein.

Synthesis of Heptalene:
Dauben and Bertelli, *J. Amer. chem. Soc.*, 1961, **83**, 4657, 4659.

Aromaticity in Inorganic Molecules:
Craig, *J. chem. Soc.*, 1959, 997.

Section 3 Crystals and X-rays

The impact of structure determination by X-rays is felt throughout the entire range of chemistry teaching from elementary to advanced level. The quantitative information on the sizes of atoms, ions and molecules, bond lengths and bond angles is fundamental to the development of chemical theory, and for this reason serious consideration must be given to the ways in which the method might be discussed even in school courses. The papers by N. Booth offer a possible approach to this problem. Successful introduction of such a course would seem to depend on an effective integration of physics and chemistry teaching—see the source-book section, page 355.

The article by K. Lonsdale is concerned with crystal structure analysis in the university undergraduate course. She gives very full details of an intensive twenty-five hour course which has been run successfully at University College, London, for the last ten years.

Another helpful article on X-rays and crystals is " X-rays, Crystals and Life ", by L. E. Alexander, in *Chemistry*, 1964, Vol. 37, No. 8, p. 6 and No. 9, p. 5.

Reprinted from *Education in Chemistry*, Vol. 1, No. 1, 1964, pp. 16-24.

CHEMICAL BONDS

I—CRYSTALS AND LATTICES

By N. BOOTH, B.SC.
H.M. Inspector of Schools

The object of this series of articles is to suggest how an approach may be made in schools to the nature of chemical bonding between atoms. It is assumed that before any work of this nature were attempted pupils would have had two or three years of a science course of an empirical nature during which they would have become familiar, largely through experiments, with a good deal of elementary physics, including especially simple current electricity and electrostatics, and similarly in chemistry with at least the properties of metals, non-metals, salts, acids, bases, water and air.

The traditional approach in school science courses to the nature of matter has been by way of the gases, with consequent emphasis on the individual isolated molecule. The use of the Avogadro Principle and the laboratory methods based on it for the determination of molecular weights, together with its extension to methods for the determination of molecular weights of species in solution, all contribute to the notion that whilst the formulation of chloroform as $CHCl_3$ is normal, in that its molecular weight as given by vapour density methods is normal, sodium chloride has an abnormal molecular weight in solution and the normal condition would be represented by NaCl.

In fact, most of the substances met and handled in a school chemistry course would by these standards be considered abnormal, and the need to be able to arrive at the structure of matter as we find and use it is clear.

To state that the formula of sodium chloride is NaCl, giving as it does merely an atom ratio and hence a weight ratio, says nothing by way either of summarization of the known properties of the compound or of helping to suggest properties as yet unknown by the pupil.

What is suggested in these articles is that it is possible to arrive at a knowledge of the structure of relatively simple substances which, taken together with a knowledge of their chemistry, will allow judgment to be used in accepting for their usefulness the models of the atoms from which the substances are formed.

COMPOUNDS OF METAL WITH NON-METAL

We can conveniently start with those compounds which result from the combination of metals with non-metals, if only because they represent the majority of substances met in most elementary courses. If we deal first with the compounds of the metals lithium, sodium etc. with the non-metals fluorine, chlorine etc. we are, by taking extreme cases, likely to get some idea of the limits attainable. That sodium and chlorine are opposites is apparent in all their physical and chemical properties, but to the young student of chemistry this is perhaps most strikingly illustrated by the actions of, say, sodium and chlorine with water—the one liberating hydrogen and the other oxygen.

At first the most obvious feature of most of the laboratory solids is that they are crystalline, and it can be shown that some at least of the powders can be obtained in crystalline form. The reactions of chalk and of calcite or Iceland spar will show their chemical identity. Gypsum may be found as crystals, but more frequently in massive form. Often the addition of water, in the form of water of crystallization, will produce crystals from a powder. Crystals may form from a molten salt, although it usually requires sudden cooling to produce recognizable crystals, as with water. More frequently they will be deposited from aqueous solution. Large crystals of potash alum and copper sulphate are commonly grown.

It is instructive to watch crystals grow and this can be very conveniently done with the aid of a filmstrip projector. A glass slide is washed in hot water, or warmed over a flame, and then dried; on it is smeared (a clean finger-tip will do perfectly well for most salts) a drop of near-saturated solution of the salt. It is now placed in the projector, and crystals will start to grow almost at once. Suitable substances include potassium chloride, sodium chlorate, copper sulphate, chrome alum and ammonium chloride. Sodium chloride will be seen to form many cubes, whilst from a solution containing urea as well, octahedra will be formed, and similarly with ammonium chloride. The introduction here of ammonium chloride, which contains no metal, should lead to a consideration of the ammonium radical and some of the properties of ammonium salts. It will be seen that not all the crystals of, say, sodium chloride have the same shape—some are cubic, some rectangular plates and so on.

Large crystals which show similar differences are simpler to observe, and quartz crystals are particularly convenient. The size of the faces and the lengths of the edges vary, but measurements on two or more quartz crystals will show that however the edges may vary in length there are corresponding pairs of faces in all the crystals and the angle between them is always the same. A simple goniometer made by taping together two 3 in. × 2 in. pieces of cellulose acetate sheet will allow the corresponding faces of two crystals to be located and the angles measured.

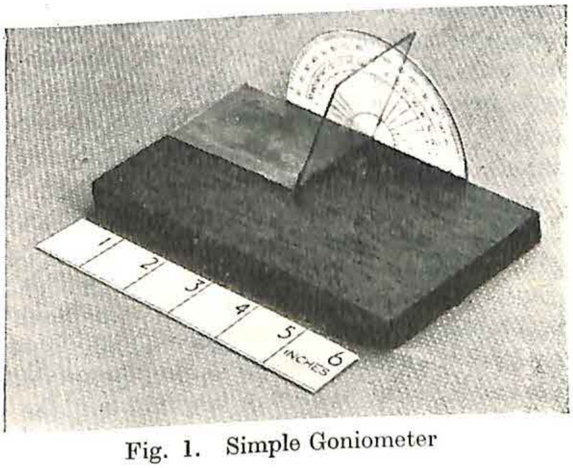


Fig. 1. Simple Goniometer

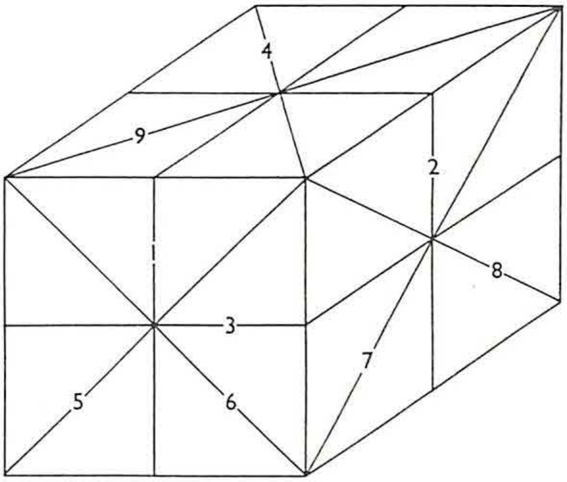


Fig. 2. The nine symmetry planes of a cube

Symmetry

It will be seen that crystals are symmetrical. It is possible to cut most of them in halves along one or more planes in such a way that each half is a mirror image of the other. Thus, a cube—such as sodium chloride, alum, potassium chloride, or sodium chlorate may form—has nine such planes of symmetry.

Crystals such as those of potassium chlorate, ferrous ammonium sulphate and gypsum have only one plane of symmetry. On the other hand some crystals have none.

There are also axes of rotational symmetry which may be demonstrated by pushing a knitting needle through cardboard models of the crystal systems (Fig. 3).

The absence of a five-fold axis of rotational symmetry in crystals should be noted and

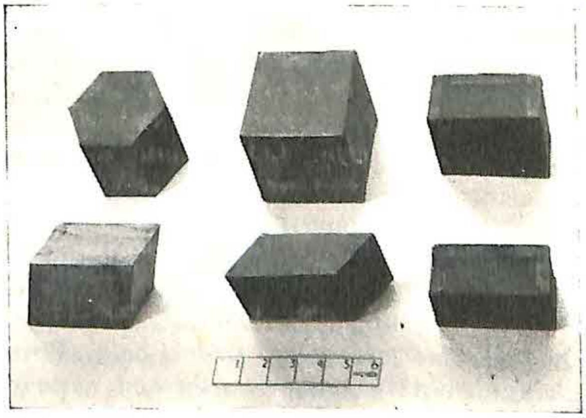


Fig. 3. The Six Crystal Systems

compared with its very common occurrence in flowers and simpler animals. The hexagonal symmetry of snowflakes can easily be seen. The ability of squares, rectangles, triangles and hexagons to fill two-dimensional space and the inability of pentagons to do the same can be shown with cardboard shapes.

Cleavage

Many crystals cleave easily along certain planes. Iceland spar, mica and gypsum are natural crystals which readily show this. Rock-salt cleaves into cubes if struck along a plane; if struck in other directions more effort is needed and the crystal breaks into fragments. Sodium chlorate crystals, which are easily grown with half-inch edges, are very suitable for demonstrating this property.

HOW ARE CRYSTALS FORMED?

Ions

Experiments with salts will lead to the hypothesis of ions. These would include the precipitation of silver chloride from aqueous solutions of the chlorine compounds of the metals; the electrolysis of molten salts such as sodium chloride (using a small proportion of calcium chloride to lower the melting point), sodium hydroxide, lead bromide, sodium nitrite; experiments which show the apparent movement of ions when the electrolysis of aqueous solutions, with a small crystal of potassium permanganate present, is projected on a screen. Sodium chloride may be taken as an example that the products of the electrolysis of the salts depend on the voltage used (or the current density) and on the nature of the electrodes. Electrolysis of the molten salt can be carried out in a porcelain boat or a crucible. An intimate mixture of pure salt with 5 per cent of calcium chloride is melted. Steel knitting needles connected to a source of 20 to 30 volts are lowered into the melt (it is advisable first to heat the tips). When an aqueous solution of the salt is electrolysed, with nichrome electrodes, hydrogen and chlorine are evolved, the chlorine attacking the anode. With nichrome and carbon, or iron and carbon, the same two gases are evolved. If, however, mercury is used as cathode no hydrogen is evolved at low voltage, but sodium amalgam is formed. The cell for this experiment may conveniently be a small Y-tube. The mercury should be clean and dry. Four to six volts will be enough.

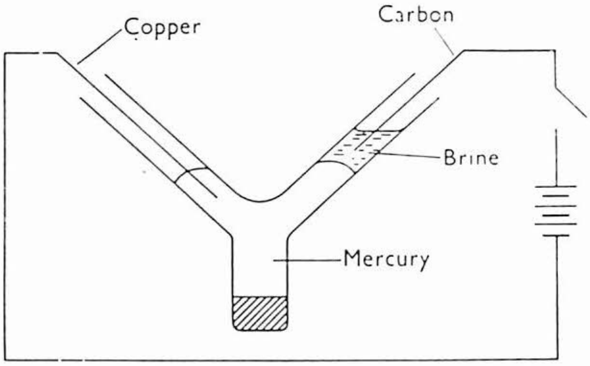


Fig. 4. Electrolysis of brine, with mercury as cathode

Models

If we accept that matter is made up of particles (and very early in a science course this will have been established, on the experimental evidence available, as a useful hypothesis) the process of crystallization is seen as the coming together of particles from their dispersion in solution or, because cooling makes it possible, from the melt. We have no way at this stage of knowing the shape of the particles and make the assumption that they are spheres, perfectly symmetrical, because we have as yet no reason to suppose otherwise and only because it is the simplest assumption to make.

We can see what happens when small spheres come together by floating expanded polystyrene spheres on water. These spheres are obtained by boiling Styrocell expandable polystyrene beads (Shell Chemical Co. Ltd) in water for a few minutes. Picked out with forceps and dropped on a water surface they will aggregate to form a raft. If spheres of the same size are used the raft is close-packed, and the hexagonal arrangement is at once observed. A larger or a smaller sphere introduced into such a raft will result in a 'lattice defect'. Reference to perforated zinc sheet, chicken wire and the honeycomb will also help to emphasize the point, which calculation will generalize, that equal circles fill an area most completely

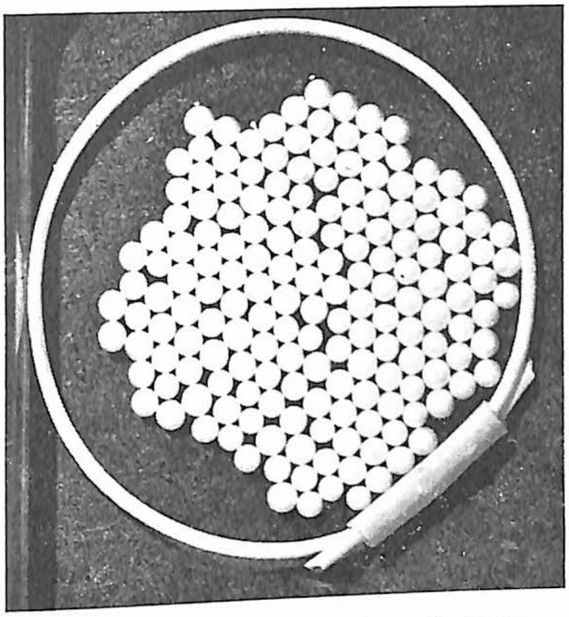


Fig. 5. Hexagonal packing of equal spheres

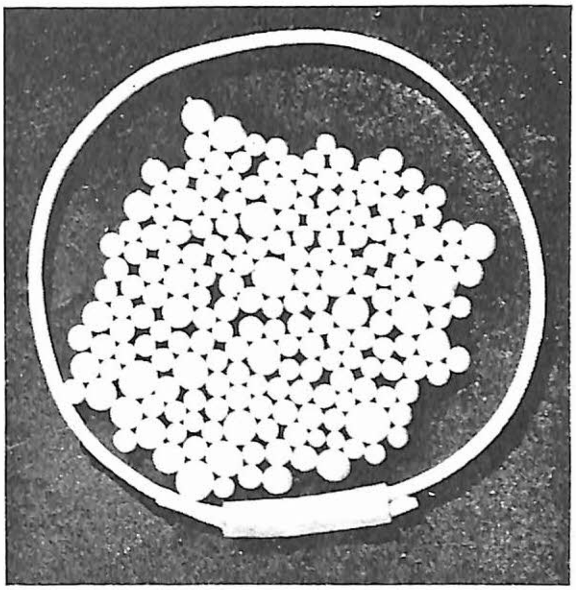


Fig. 6. Lattice defect when a large sphere is interposed

when they take up the hexagonal arrangement.

But, except in surface films, matter exists in three dimensions, and to show how spheres are packed together to fill three dimensions we can use table-tennis balls (expensive at 4*d.* each minimum), wooden spheres which can be purchased in several sizes from 'Do-it-yourself' shops and cost 1*s.* 6*d.* a dozen, polythene spheres or expanded polystyrene spheres. These last can be made at very low cost from expanded polystyrene building-board off-cuts, which many manufacturers will supply. The boards may be cut with a sharp knife, or a hot wire or knife, into cubes, the corners trimmed off and the resulting block rubbed down into a sphere on fine glass paper. If desired, they may be coloured by any water-soluble dye. Drawing inks are very satisfactory, diluted by about six parts of water. Polystyrene spheres in various sizes can be obtained from Elford Plastics, Elland, Yorkshire.

The lattices shown are made from wooden spheres of 1 in. diameter. The spheres are cemented together by an impact adhesive to form close-packed rafts, and the rafts themselves cemented together to make different lattices. Of the two shown in Fig. 7 the one on the left is a face-centred cubic lattice and that on the right a simple hexagonal lattice. In the face-centred lattice the close-packed hexagons can be seen in planes inclined to the horizontal, whilst in the hexagonal lattice they occupy horizontal planes.

The method of construction of the lattices can be demonstrated by placing table-tennis balls in a Perspex cube of side 6 in.

Fig. 8 shows the face-centred arrangement so constructed, with one of the close-packed rafts coloured to emphasize the layers. In Fig. 9, taken from the opposite side of the cube, three layers have been removed to reveal one of the hexagons from which the whole lattice is constructed.

Now, the way crystals grow and the fact that they have cleavage planes suggests that their external symmetry is the result of an internal symmetry. How may this be verified and the internal pattern deduced?

Diffraction

Visible light passing through a transparent screen with a fine pattern may be so affected that its appearance after passing through the screen tells us the shape of the pattern and its spacing. The simplest example is a diffraction grating consisting of a transparent sheet on which a series of closely-spaced parallel straight lines have been ruled. If

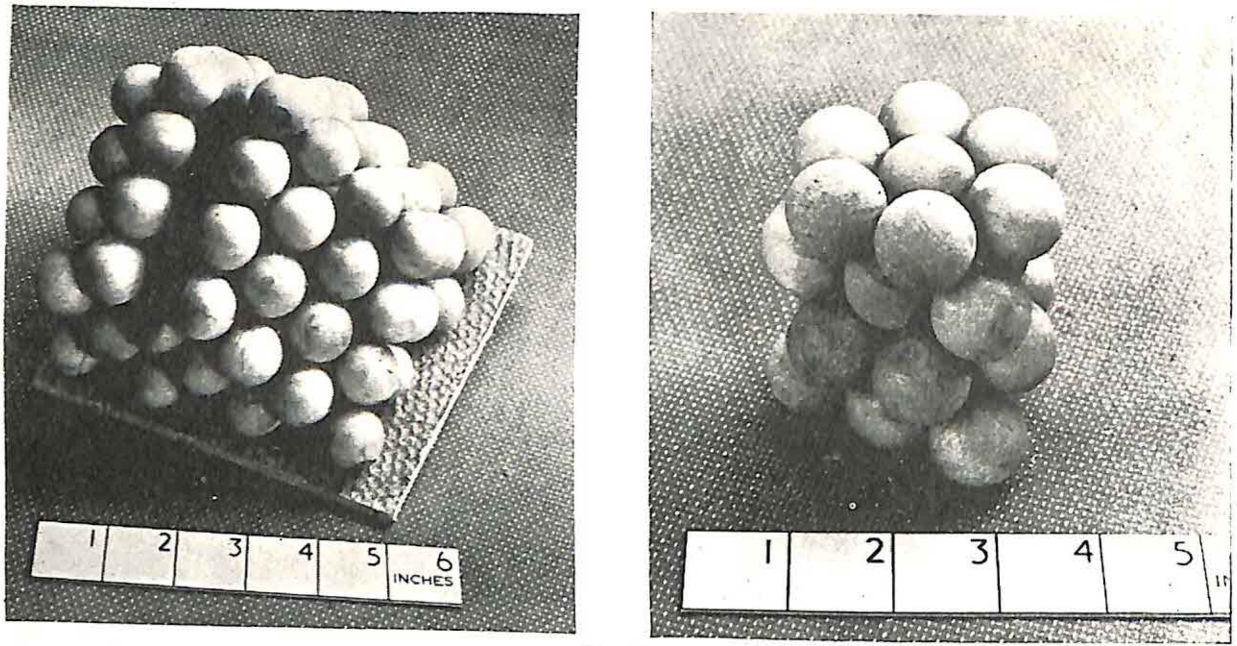
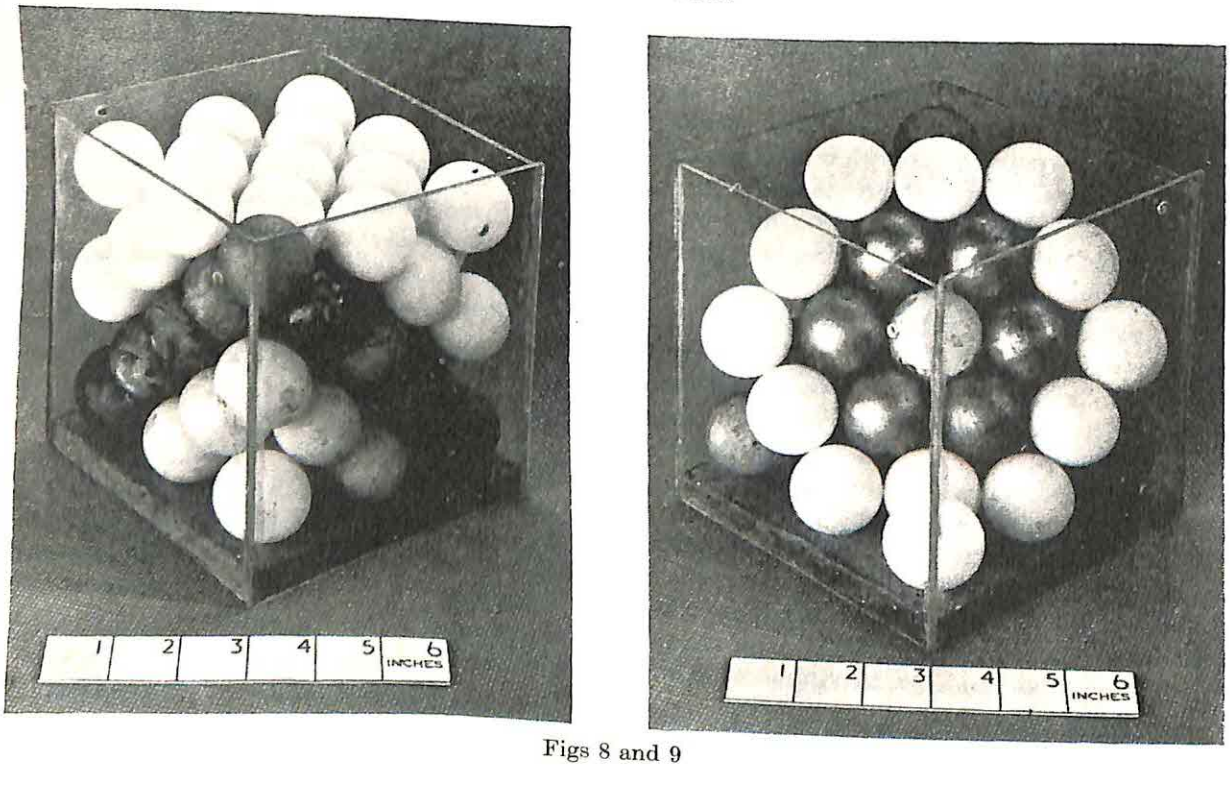


Fig. 7

light incident on the grating is in the form of a small spot of monochromatic light, the emergent light is a series of small spots separated by dark spaces. The light has been spread out not uniformly. Turning the grating at right angles to its first position will cause the pattern of spots also to turn through a right angle; thus the first feature of the screen's pattern can be decided. The pattern of spots is spread out in a direction which depends on the direction of the lines on the sheet. If the light is viewed at an oblique angle along the surface of a gramophone record it will be seen that the pattern of spots is at right angles to the grooves on the record.



Figs 8 and 9

We can learn a good deal about how gratings act, and of the uses to which they can be put, from a model consisting of a board, 60 cm long and 50 cm wide, covered with white plastic sheet (Fig. 10). A centre line is drawn to divide it along its length, and two parallel lines are drawn along the width 2 cm and 8 cm from each end, respectively. The line 2 cm from one end is drilled at 2-cm intervals, except that the centre spot is left undrilled. Two aluminium strips, each 2 cm wide, are cut to make combs, the centres of the gaps (or the centres of the teeth) being 2 cm apart. A plug terminal at one end of each strip fits into the holes drilled in the board.

Starting with the plugs 4 cm apart, the strips are brought together along the line 8 cm from the distant end of the board. Two gaps in the combs coincide. Now the combs are swung together in either direction until gaps once more coincide on the line. In fact, with the 4-cm spacing the next coincidence is off the board. Now the plugs are separated by 8 cm, 12 cm, 16 cm and so on, and points of coincidence marked on a strip of cardboard laid along the 8-cm parallel. Distances from the centre line are measured.

A. *2-cm gap spacing*

Plug Spacing (cm)	Points of Coincidence (cm)				
8	12·7				
12	8·2	17·3			
16	6·2	12·7	20·1		
20	4·9	10·3	15·8	22·1	
24	4·1	8·3	13·1	18·0	23·4
28	3·6				
32	3·3				

B. *4-cm gap spacing*

Plug Spacing (cm)	Points of Coincidence (cm)	
12	17·3	
16	12·7	20·1

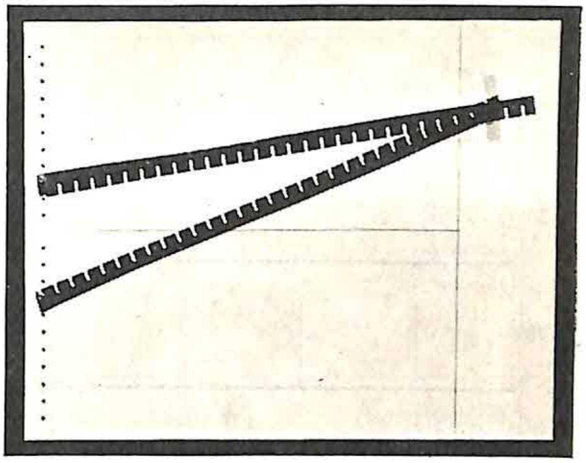


Fig. 10

A graph (*see* Figs 11 and 12) can be drawn of points of first coincidence against plug spacing, and from this it is possible to deduce the plug positions—even if they cannot be seen—by measuring the point of first coincidence and referring to the graph. The model will also show that if the gap spacing is much greater than the plug spacing no pattern will be obtained, and this also happens if the gap spacing is much smaller than the plug spacing. It will be seen, too, that the smaller the spacing the greater the separation of the points of coincidence.

If a point of light is viewed through a handkerchief in a darkened room a four-pointed pattern is seen. A fine-mesh wire-gauze will give the same effect—about 120 mesh is suitable. Tilting the gauze or handkerchief will again cause the pattern to be elongated in the direction in which the gap is narrowed. Deformation of the grating produces a new pattern.

We can learn, then, about the pattern of a grating from the diffraction pattern produced when light passes through it. The production of a diffraction pattern is itself evidence that light has wave properties, and the model we used suggests that the wavelength of the light will have to be somewhere near the spacing of the pattern. Experiments with a ripple tank will confirm this. Similar effects can be obtained from three-dimensional gratings provided the wavelength used is about the same as the spacing of the planes of the grating. The lattices shown in

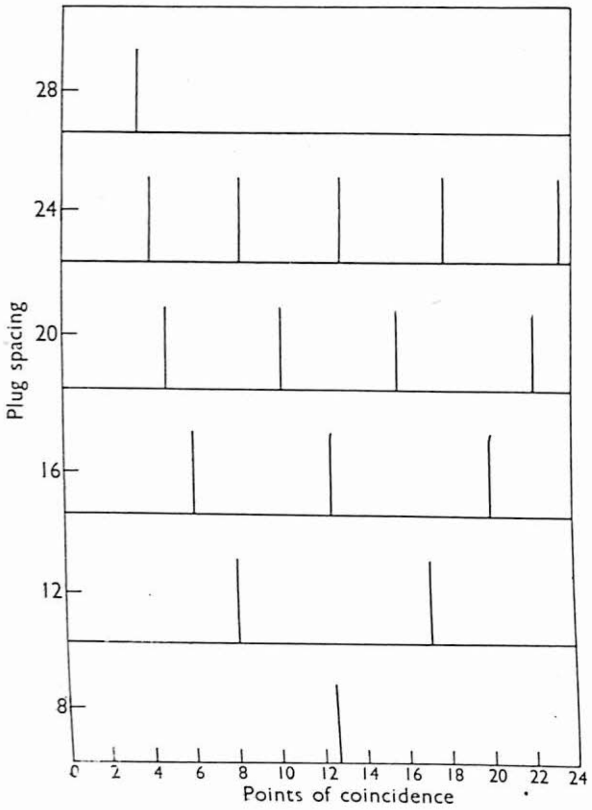


Fig. 11

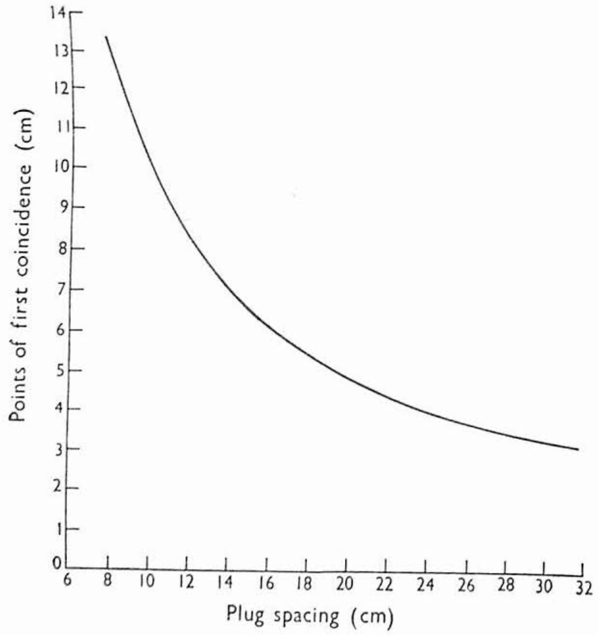


Fig. 12

Fig. 7 are suitable for this purpose. The spacing of the close-packed layers will be about 2·5 cm, and the 3-cm generators and receivers now coming into use in school physics courses can be used to produce patterns which allow the different modes of stacking the rafts to be distinguished. A lattice is mounted about 50 cm from the transmitter and the receiver moved round an arc of a circle of radius 50 cm and centred on the centre of the lattice. Readings are taken every 0·25 radians of arc moved by the receiver. Runs are carried out first with no lattice present and then with the lattice set in four different positions chosen at random in three dimensions. Results are shown on the accompanying graphs (Fig. 13). Compare results given by a hexagonal lattice (Fig. 14).

If, in fact, crystals are a regular arrangement of particles in, as seems possible, the cleavage planes, we know from experiments to determine the thickness of surface films that the particles must be very small.

This can be very effectively and simply demonstrated. Flowers of sulphur are sprinkled on the surface of clean water in a tray with 50-cm sides. A glass rod is drawn out to a fine point and the tip slightly rounded. The tip is *touched* on the surface of a drop of camphorated oil and then on the centre of the water in the tray. The large area of the resulting clear circle compared with the minute volume of the drop of oil is very striking.

Typical results of surface-film measurements show that the thicknesses are of the order of 10 Å. The layers in a crystal could be expected, therefore, to be separated by about this distance, and any radiation we use to test this hypothesis and to determine where the layers lie, and how far apart they are, must have a wavelength of about this order. In fact, X-rays are found to be suitable. It will be seen from the results obtained with the wooden-sphere lattice that the pattern depends on the orientation of the lattice or, in other words, on the planes in the lattice which are reflecting the beam of radiation; and the same applies when a pattern is obtained by passing X-rays through crystals. The photograph, Fig. 15,

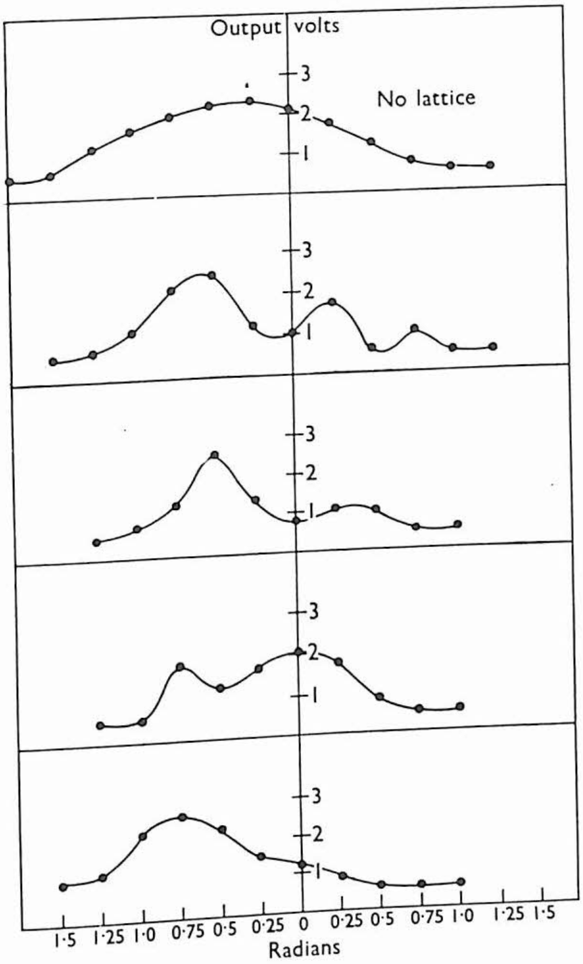


Fig. 13.

shows an X-ray diffraction picture obtained with a phosphorus compound in one particular orientation.[2] The regular pattern of spots strongly suggests a regular internal pattern.

Simple mathematical analysis shows that we shall get reinforcement of the diffracted X-rays when a set of planes is at such an angle to the incident beam that the path difference of rays reflected from successive planes is an integral number of wavelengths. The pattern shown in Fig. 15 was obtained by slowly oscillating a crystal through 15° while it was irradiated with monochromatic X-rays. The spots correspond to planes in the crystal lattice which are at the correct angle to the incident beam for reinforcement to occur.

The 3-cm generator and receiver can be used as described by Dr P. J. Beckett[1] to verify this for 3-cm waves.

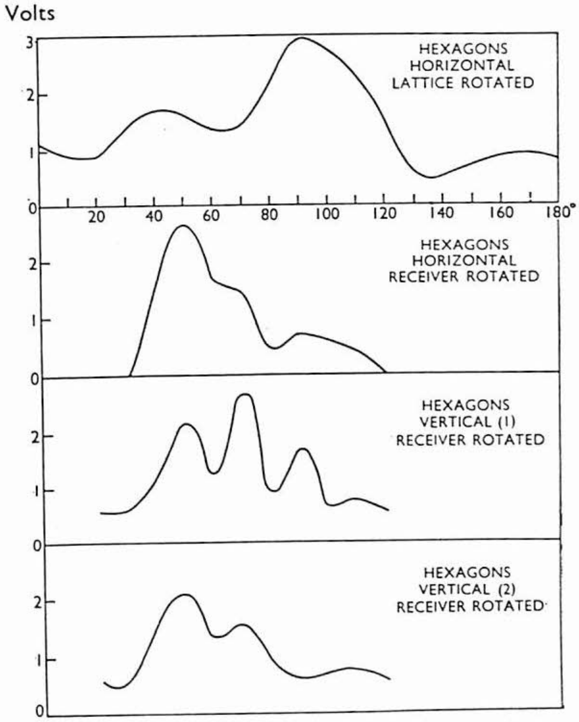


Fig. 14.

The discovery by von Laue in 1912 of the diffraction of X-rays by crystals is one of the major advances in science. It led on the one hand to the immediate development of X-ray

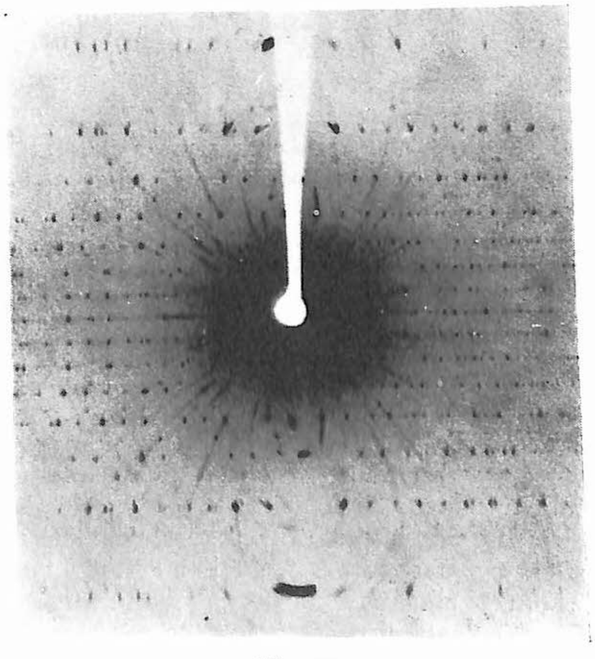


Fig. 15

spectroscopy, from which came such fundamental contributions to the theory of the structure of matter as, for example, the idea of atomic number, and, on the other hand, it provided a method for determining the arrangement of ions, atoms and molecules, not only in simple structures but also in those of great complexity.

The greatest triumph of nineteenth-century chemistry had, perhaps, been the establishment of the position of the atoms in a vast number of organic compounds, and the proof that the properties of a compound depend very much on the arrangement in space of its components. There were, however, no methods available for achieving the same knowledge in the case of the great majority of inorganic compounds, and it was in this field that the first advances resulting from the use of X-rays were made. Since then the method has been applied to the elucidation of the arrangement of atoms in minerals of great complexity, such as the silicates in inorganic chemistry, and, most complex of all, the biological molecules.

Much of the earlier work of the X-ray crystallographer had the effect of confirming and of giving precise measurement to the previous concepts of chemists. Now, however, the methods are so well developed that it is possible to establish the structures of molecules of such complexity as to be beyond the scope of analytical chemistry.

In the next article in this series I shall show how the method of X-ray crystallography gives precise information about the nature of the particles, their arrangement and their sizes, in the crystals of the chlorides of the alkali metals.

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1. 'The simulation of X-ray crystallography using micro-waves,' *School Science Review*, No. 153, pp. 441-3.

2. X-ray photograph of $P_4N_4(OMe)_8$ by Dr G. J. Bullen, Birkbeck College, London.

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CHEMICAL BONDS

II—X-RAYS AND THE ALKALI-METAL CHLORIDES

By N. Booth, B.Sc.
H.M. Inspector of Schools

POWDER CRYSTALLOGRAPHY

In a crystal the reflecting planes are fixed in position and, since the distance a ray has to travel between planes depends on the spacing of the planes and on the angle at which the ray is incident on them, it will be mere luck if the orientation of the crystal is such as to give a diffracted beam. One way of getting over this is to oscillate or rotate the crystal; another, which also allows very small crystals to be used, is the method of X-ray powder crystallography. By using many crystals in this way there will always be at least one in the right position to give a diffracted beam. A diagram (Fig. 1) will illustrate this for two crystals.

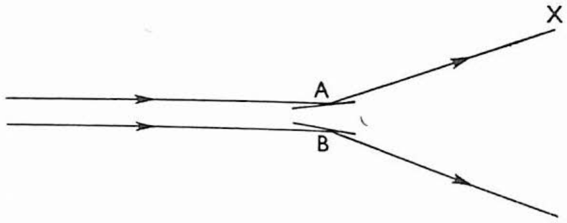


Fig. 1

If crystal A is in the position to give a diffracted beam in the direction AX, then crystal B will do the same along BY. Considered in three dimensions, it will be seen that the result is a 'cone of diffraction.' Yet other crystals will produce similar effects from other sets of planes and, because both plane-spacing and angle of incidence will be different, the apex angles of the cones will differ.

Five examples of the pattern obtained by this method are shown in the photographs (Fig. 2). The film is wrapped round to form a cylinder with the powder specimen at its centre and the beam of X-rays enters the camera at the dark spot on the left and emerges at that on the right, which in the camera is diametrically opposite. The lines on the photographs are arcs of the circumferences of the bases of the cones described above. The dimensions of the camera are such that the circumference of the film in the camera is 360 mm. Reference to Fig. 1 will show that if the glancing angle between the X-ray beam and the crystal plane is θ, then the apex angle of the cone is 4θ.

$$\text{Now } 2\pi \times \text{Radius of Camera} = 360 \text{ mm}$$
$$\therefore \text{Radius of Camera} = 180/\pi \text{ mm}$$

It is sufficient for our purpose to concentrate on the rays diffracted through small angles, that is to say on those arcs on the photographs which are centred on the right-hand spot, and for each of these circles we have:

$$\text{Diameter of Circle} = \text{Radius of Camera} \times 4\theta$$
$$= 180/\pi \times 4\theta$$

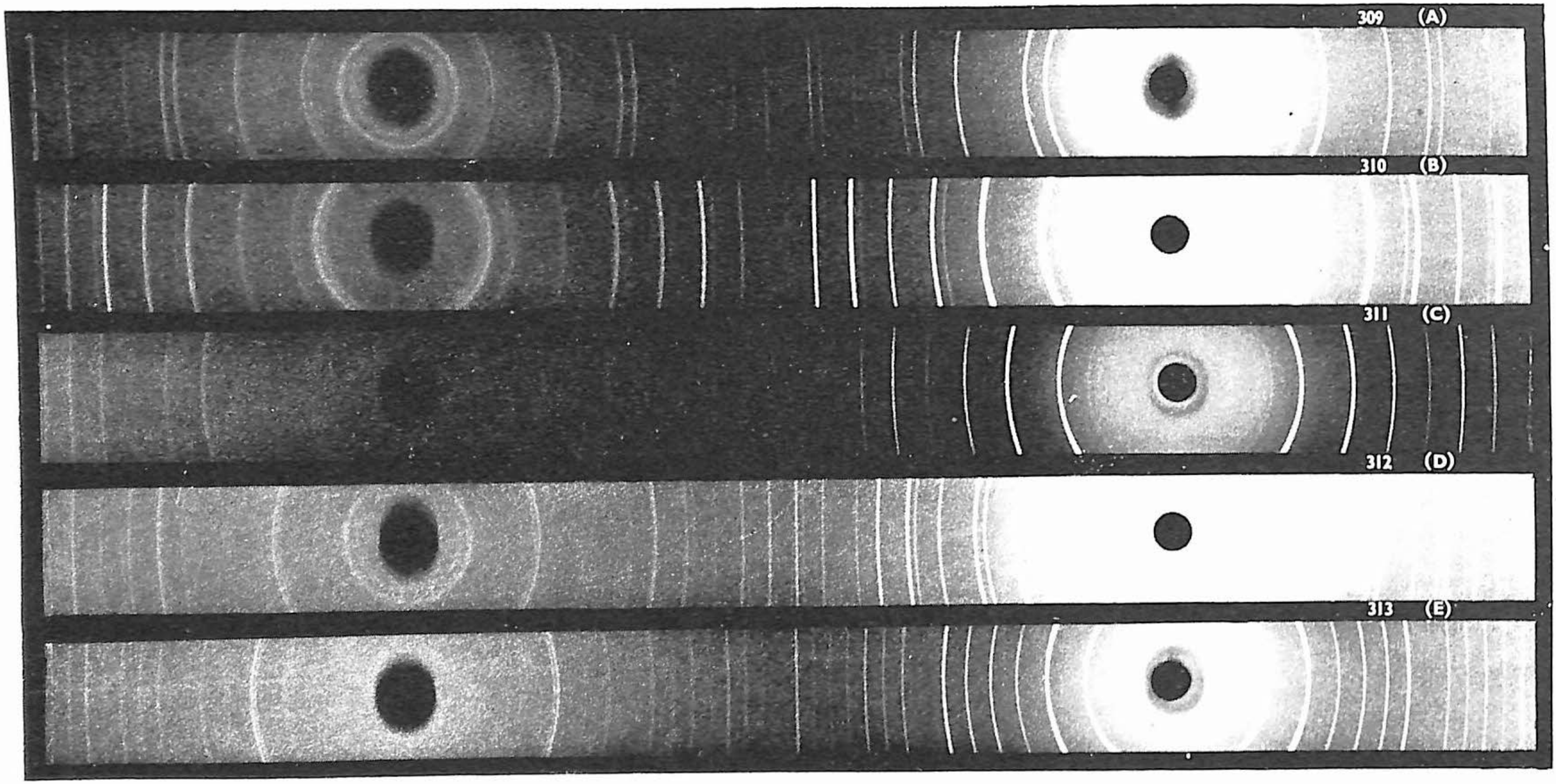
where the diameter is in millimetres and θ in radians.

$$\text{Therefore } 4\theta = \text{Diameter} \times \frac{\pi}{180} \times \frac{180}{\pi} \text{ degrees}$$

i.e. 4θ in degrees = Diameter in millimetres

The angle of diffraction, θ, can therefore be measured on the photographs.

The five salts whose photographs are shown are, in order, reading down: the chlorides of lithium, sodium, potassium, rubidium and caesium. Merely by looking at the photographs it is possible to infer that (*a*) each salt has a regular internal pattern; (*b*) the patterns for lithium, sodium and rubidium chlorides are very much alike; the other two are different from these but are similar to each other; (*c*) the patterns for lithium, sodium and rubidium chlorides, although similar, are not identical. The same lines are present in each, but corresponding lines are closer to the central spot and closer to their neighbours as we descend the series. Remembering the experiment



[*Photographs by J. Eyett, Department of Geology, University of Nottingham.*

Fig. 2. Powder photographs of the alkali-metal chlorides: (A) lithium; (B) sodium; (C) potassium; (D) rubidium; (E) caesium.

with the board, described in the first article in this series (*Educ. Chem.*, **1** (1), 21), we could account for the changes of pattern for these three chlorides if the planes causing the patterns were identically arranged, but were getting further apart as we went from lithium to rubidium; (*d*) the internal symmetry of each is cubic; and the next question to tackle is—How do we know this?

CUBIC SYMMETRY AND X-RAY DIFFRACTION

Lattices

Since each salt crystallizes in the form of cubes, it is perhaps not surprising that the internal symmetry should also be cubic and analysis of the patterns makes it quite certain that this is so. As we have seen from the model diffraction gratings previously examined, it is from the spacing of the lines in the diffraction pattern that this deduction can be made.

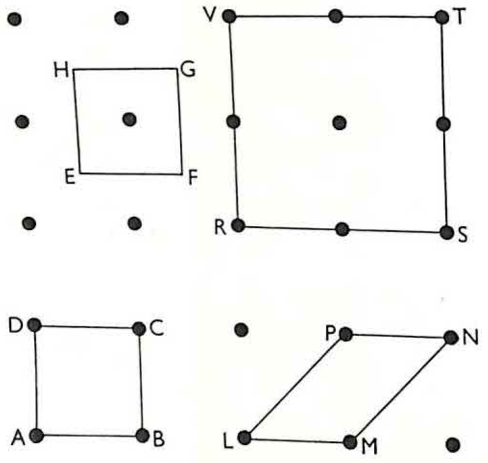


Fig. 3

Consider first a pattern of particles in two dimensions (Fig. 3). The pattern can be divided into sets of identical squares, rectangles or, in general, parallelograms, of which four examples are drawn. Such parallelograms are called unit cells, and any one of the infinite number of possibilities could be chosen as the unit of this pattern. Note that ABCD contains the equivalent of one point of the pattern (or lattice), and so do EFGH and LMNP, whilst RSTV contains four.

Since we can define this lattice by rectangular axes it will be simpler to do so and choosing one of, for example, ABCD, EFGH or RSTV allows us to generate the lattice by equal translations of the unit cell along each axis. As EFGH illustrates, the origin of the repetition lattice can be chosen quite arbitrarily so that the lattice points are not necessarily associated with any particular sets of particles in the actual structure.

Exactly similar considerations apply to a three-dimensional lattice, in which the unit cell is, in general, a parallelepiped.

Rational Lines and Planes

As the line XY (Fig. 4) shows, a line passing through one point in a lattice will not necessarily pass through any other point. If it passes through two points, then, as RST and RPQ show, and as simple geometry will readily confirm, it must pass through an infinite number of points in a lattice of infinite extent. This is simply because any such line is either the side or diagonal of a square or rectangle. Such lines are called *rational lines*. Similarly it can be shown, or seen on a model, that in an infinite three-dimensional lattice any plane passing through

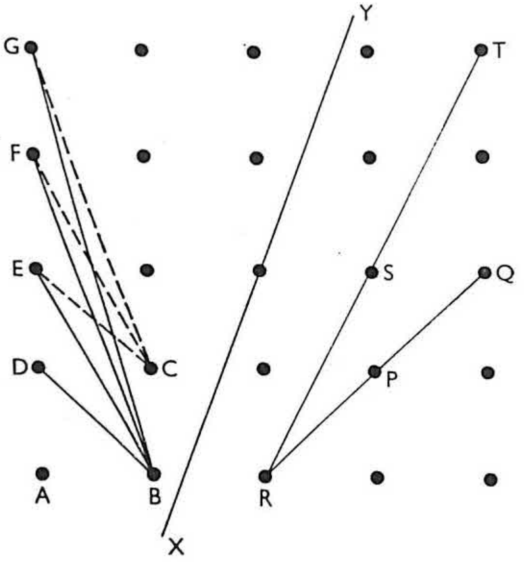


Fig. 4

three points which are not colinear will also pass through an infinite number of lattice points. These are called *rational planes.* Movement of a rational line or plane along the axes of the lattice by the unit-cell distance will generate a family of parallel lines or planes whose separation will be the same as the distance of the first line or plane from the lattice origin.

In the two-dimensional lattice of Fig. 4 the rational lines BD, BE, BF and BG divide the horizontal translation distance CD by 1, 2, 3 and 4 respectively. Each of the pairs BD and CE, BE and CF, BF and CG illustrates the point that each of a family of rational lines has the same intercept on the side of a unit cell. What is more, because it is a lattice (and so AD=DE=EF=FG *etc.*), the divisor in each case must be a whole number.

Precisely the same considerations apply to the rational planes of a three-dimensional lattice, and a plane is identified by the divisor along each axis, the divisors being given the general labels h, k, l, which are known as the Miller Indices.

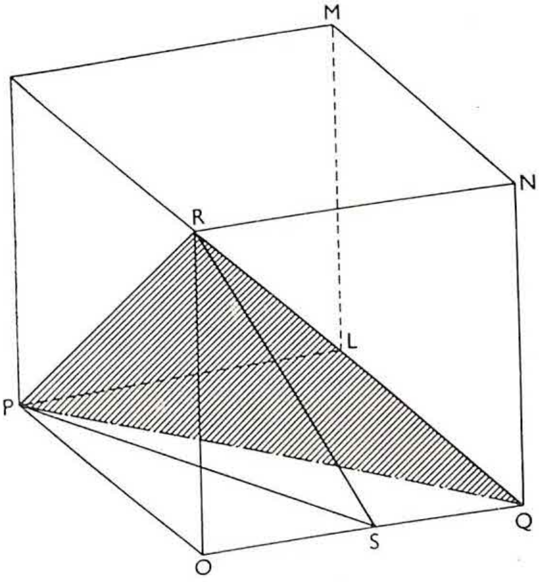


Fig. 5

Thus in Fig. 5 the values of h, k and l for the plane PRQ are each unity or, more briefly, it is a 1, 1, 1 plane, written (111). PSR is a (211) plane and LMNQ is a (100) plane.

Interplanar Spacing in a Cubic Lattice

A solid model (Fig. 6) will simplify the calculation. The plane ABC makes intercepts OA, OB and OC along the edges of the cube. ON is the perpendicular from the corner of the cube to the plane ABC. Ox, Oy and Oz are the co-ordinates of N with respect to O.

Then
$$\frac{\mathrm{ON}}{\mathrm{OA}} = \frac{\mathrm{O}x}{\mathrm{ON}}$$
and
$$\frac{\mathrm{ON}}{\mathrm{OB}} = \frac{\mathrm{O}y}{\mathrm{ON}}$$
$$\frac{\mathrm{ON}}{\mathrm{OC}} = \frac{\mathrm{O}z}{\mathrm{ON}}$$
But
$$\mathrm{ON}^2 = \mathrm{O}x^2 + \mathrm{O}y^2 + \mathrm{O}z^2$$
and it follows that
$$\frac{1}{\mathrm{ON}^2} = \frac{1}{\mathrm{OA}^2} + \frac{1}{\mathrm{OB}^2} + \frac{1}{\mathrm{OC}^2} \quad .. \quad (1)$$
If the length of the side of the cube is a,

then
$$h = \frac{a}{\mathrm{OA}} \quad k = \frac{a}{\mathrm{OB}} \quad l = \frac{a}{\mathrm{OC}}$$
and substitution in (1) above gives
$$\frac{1}{\mathrm{ON}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$
But ON $= d$, the spacing of the planes of this family.
$$\therefore d = a/\sqrt{h^2 + k^2 + l^2} \quad .. \quad .. \quad (2)$$

Bearing in mind that h, k and l are either zero or integers, we can now draw up a list (Table I) of possible values for d.

TABLE I

hkl	$h^2 + k^2 + l^2$	d
100	1	a
110	2	$a/\sqrt{2}$
111	3	$a/\sqrt{3}$
200	4	$a/2$
210	5	$a/\sqrt{5}$
211	6	$a/\sqrt{6}$
220	8	$a/\sqrt{8}$
221 300	9	$a/3$

It can be seen that there is no value of $d = a/\sqrt{7}$, and nor is there for $a/\sqrt{15}$, $a/\sqrt{23}$, $a/\sqrt{28}$, etc.

This at once gives us a possible means of determining whether or not a given crystal

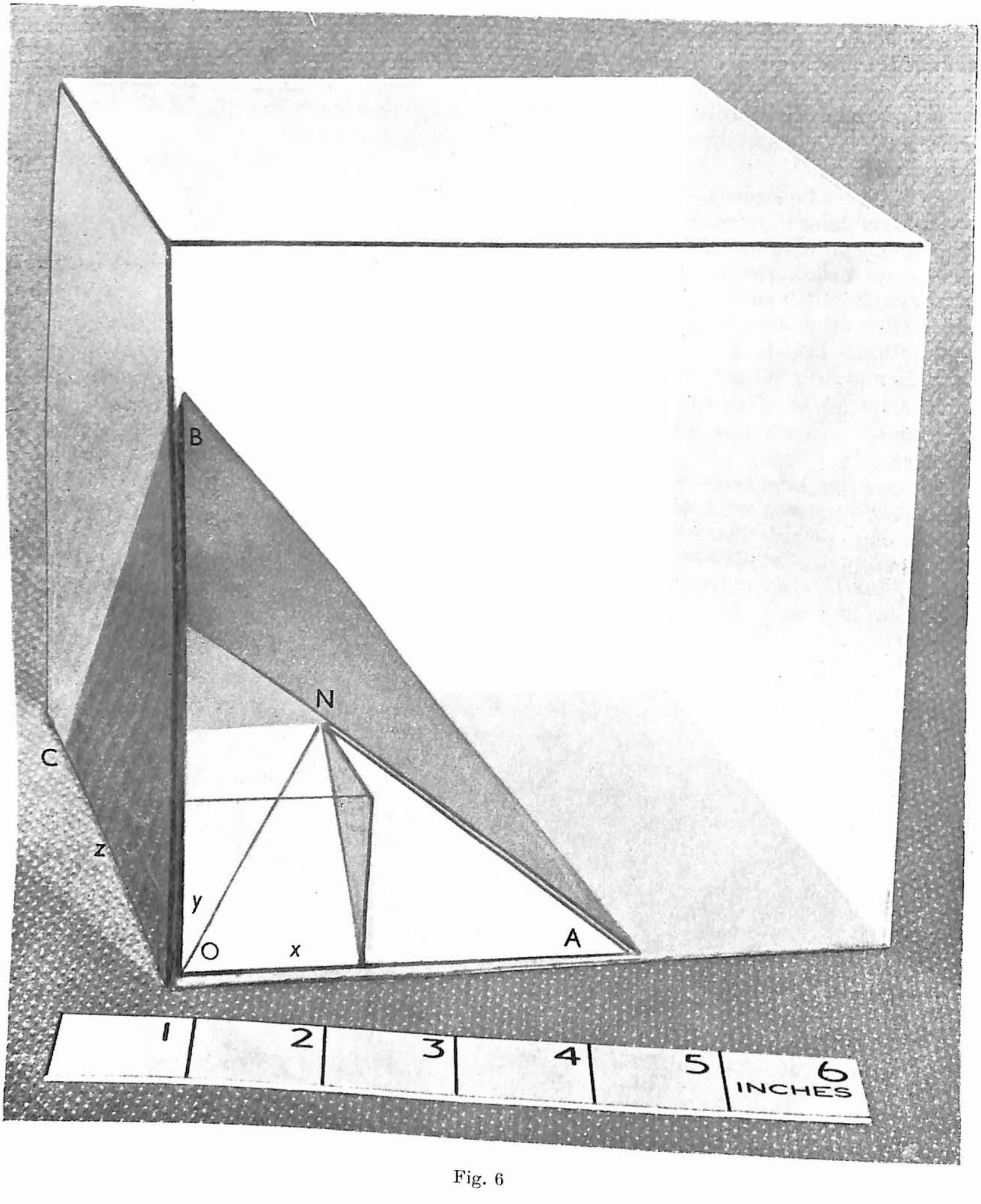


Fig. 6

has an internal structure which can be represented by a cubic lattice, since similar calculations for other geometrical units from which space-filling lattices can be constructed give an entirely different expression for d.

X-RAY DIFFRACTION AND THE LATTICE PLANES

Now the geometry of reflection from parallel planes and experiments with the 3-cm equipment described earlier (*Educ. Chem.*, **1** (1), 23), show that reinforcement will occur when $n\lambda = 2d \sin \theta$, where n is an integer, λ the wavelength of the radiation, d the plane-spacing and θ the glancing angle. It is usual to take n as unity, since the nth order of diffraction from the hkl plane may be considered as the first order ($n = 1$) from the plane nh, nk, nl. This is only to say that the same value of sin θ will be obtained by halving d as by doubling n. The expression then becomes

$$\lambda = 2d \sin \theta$$

or

$$\sin^2 \theta = \lambda^2/4d^2$$

Substituting for d^2 from (2) above gives

$$\sin^2 \theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

Thus, if λ and a are constants we have $h^2 + k^2 + l^2$ proportional to $\sin^2 \theta$. We have seen how 4θ, and hence $\sin^2 \theta$, can be obtained by measuring the diameter in millimetres of the circles on the X-ray photograph, and we have also seen that, because h, k and l are integers, the values of $h^2 + k^2 + l^2$ must also be integral, so that we now have a simple way of finding the value of $h^2 + k^2 + l^2$ for each pair of lines on the photographs. All that has to be done is to find the ratio of the values of $\sin^2 \theta$, which will be the same as the ratio of the values of $h^2 + k^2 + l^2$, and scale them up to give integral values.

Thus, on photograph A for lithium chloride, the distance between the first pair of lines each side of the right-hand spot is 60 mm. Hence θ is 15° and $\sin^2 \theta$ is 0·06691. For the second pair the distance apart is 69·5 mm; θ is therefore 17·4° and $\sin^2 \theta$ is 0·08940. These values of $\sin^2 \theta$ (and hence of $h^2 + k^2 + l^2$) are in the ratio of 1 to 1·336, or, to bring both to whole numbers, 3 to 4.

THE STRUCTURE OF THE ALKALI-METAL CHLORIDES

The results obtained for all five salts for angles of diffraction less than 45° are shown in Table II (overleaf).

It will be seen later that caesium chloride is of particular interest and for this salt the fourth column continues as follows: 11·87, 12·85, 13·86, 15·86, 16·86, 17·82, 18·79, 19·96, 20·87, 21·97, 23·96. Taken to the nearest integer this becomes: 12, 13, 14, 16, 17, 18, 19, 20, 21, 22, 24. Note that 15 and 23 are missing but that 14 is present.

One statement can be made at once—in none of the ($h^2 + k^2 + l^2$) columns do the values 7, 15 or 23 appear, and we may be sure therefore that the internal symmetry in each case is indeed cubic.

We have also confirmed the earlier deduction, made from the appearance of the photographs, that lithium, sodium and rubidium chlorides form one group and potassium and caesium chlorides another. All possible lines are in fact present for the second group, several are missing from the first. We may take it, then, that because their diffraction patterns are similar so are the internal structures of lithium, sodium and rubidium chlorides on the one hand, and of potassium and caesium chlorides on the other—not forgetting that both groups are still cubic, and this will be considered later.

THE UNIT CUBE

It is possible now to obtain direct checks that we are on the right lines.

From the expression $\lambda = 2d \sin \theta$ it follows that d is proportional to $1/\sin \theta$.

Consider the (220) and (311) planes for the three salts of the first group (Table III).

TABLE III

hkl	Values of $1/\sin \theta$		
	LiCl	NaCl	RbCl
220	2·357	2·613	3·033
311	2·015	2·203	2·586

TABLE II

A. *Lithium Chloride*

4θ (mm)	$\theta°$	$\sin^2 \theta$	Ratio	$h^2 + k^2 + l^2$	hkl
60	15	0·06691	1	3	111
69·5	17·4	0·08940	1·336	4	200
100·5	25·1	0·1799	2·689	8	220
119	29·75	0·2470	3·692	11	311
125	31·25	0·2698	4·008	12	222
147	36·75	0·3588	5·351	16	400
160·5	40·1	0·4149	6·200	19	331
168	42	0·4476	6·689	20	420

B. *Sodium Chloride*

55	13·75	0·05650	1	3	111
63	15·75	0·07370	1·305	4	200
90	22·5	0·1464	2·592	8	220
108	27	0·2061	3·649	11	311
113	28·25	0·2226	3·941	12	222
132	33	0·2965	5·248	16	400
146	36·5	0·3535	6·258	19	331
150	37·5	0·3706	6·560	20	420
167	41·75	0·4434	7·848	24	422

C. *Potassium Chloride*

56·5	14·1	0·05933	1	1	100
80·5	20·1	0·1181	1·991	2	110
100	25	0·1786	3·010	3	111
117	29·25	0·2393	3·942	4	200
132·5	33·1	0·2982	5·025	5	210
146·5	36·6	0·3555	5·991	6	211
174	43·5	0·4739	7·987	8	220

D. *Rubidium Chloride*

77	19·25	0·1087	1	8	220
91	22·75	0·1495	1·375	11	311
95·5	23·9	0·1641	1·510	12	222
110	27·5	0·2132	1·962	16	400
122	30·5	0·2575	2·369	19	331
126	31·5	0·2730	2·512	20	420
139·5	34·9	0·3216	2·959	24	422
149	37·25	0·3664	3·371	27	333 511

E. *Caesium Chloride*

43	10·75	0·03482	1	1	100
61	15·25	0·06830	1·961	2	110
75	18·75	0·1034	2·969	3	111
87·5	21·9	0·1391	4·003	4	200
98·5	24·6	0·1733	4·976	5	210
108·5	27·1	0·2074	5·955	6	211
127·5	31·9	0·2792	8·017	8	220
136	34·0	0·3127	8·980	9	221
144·5	36·1	0·3471	9·965	10	310
152·5	38·1	0·3807	10·93	11	311

The plane-spacing, d, increases as we go from lithium to rubidium chloride, and the reasonable assumption is that a structural unit of rubidium chloride is larger than that of sodium chloride, which is itself larger than that of lithium chloride.

Now consider the (200) and (220) planes for potassium and caesium chlorides (Table IV).

TABLE IV

hkl	Values of $1/\sin\theta$	
	KCl	CsCl
200	2·046	2·681
220	1·452	1·893

Again d increases from potassium to caesium; again, if we consider the values for the (220) planes in all five cases, the difference between the two groups is made very clear.

Consider now the expression

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

For the same family of planes, in the different salts, since λ and hkl are the same, we have $a \propto 1/\sin\theta$, where a is the side of the unit cube.

Thus the volumes of the unit cubes in each case are in the same ratio as $1/\sin^3\theta$ for each salt. For the salts of one group, each having the same internal structure, we should expect that the values of the quotients, formula weight/volume of unit cube, would be in the same ratio as that of the densities of the salts, and since $a^3 \propto 1/\sin^3\theta$, we should expect from the foregoing that the values of formula weight $\times \sin^3\theta$ would be in the same ratio as the densities of the salts. The results obtained are given in Table V.

TABLE V

Salt	LiCl	NaCl	RbCl
Density	2·07	2·18	2·80
Ratio of densities . .	1	1·05	1·35
Formula Wt $\times \sin^3\theta$ for (220) planes . .	3·24	3·28	4·37
Ratio	1	1·01	1·35

For the 311 planes the ratio is 1 : 1·06 : 1·34.

The agreement is certainly good enough to support the contention that the X-ray photographs can give detailed information about the structure of these salts.

Similar calculations for the (100) and (110) planes of potassium and caesium chlorides give ratios of 1·00 and 1·01 as compared with a density ratio of 1·99. These results suggest that there are the same number of formula weights of lithium, sodium and rubidium chlorides in a unit cube of each salt but that there are twice as many formula weights of potassium chloride as of caesium chloride in their respective unit cubes. The result will have an important bearing on the models of the five salts we ultimately construct.

SIMPLE, FACED-CENTRED AND BODY-CENTRED CUBIC LATTICES

If a lattice is constructed from units which are cubes, each with one particle at the corner of each cube, the result is shown in Fig. 7.

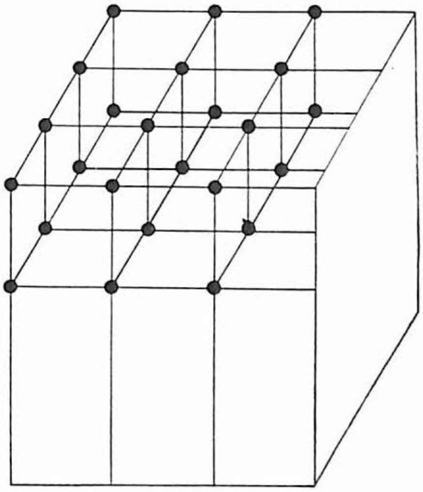


Fig. 7

Each of the corner particles is shared by the eight surrounding cubes and thus each unit cube contains one particle or one lattice point. Such a lattice is a simple or primitive cubic lattice. A crystal so constructed would be expected to give all possible lines on its X-ray diffraction photograph. There are, however, two other ways in which points can be arranged in cubic lattices. In the *body-centred* cubic lattice an extra particle is placed at the centre of each simple cube (*see* Fig. 8) and in the *face-centred* lattice a particle is added at the centre of each face (*see* Fig. 9).

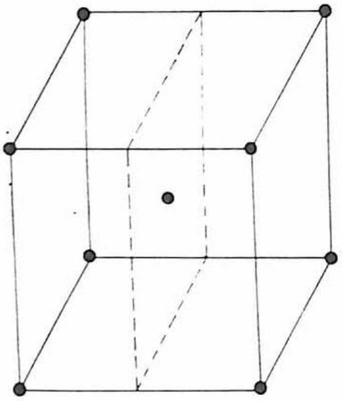


Fig. 8

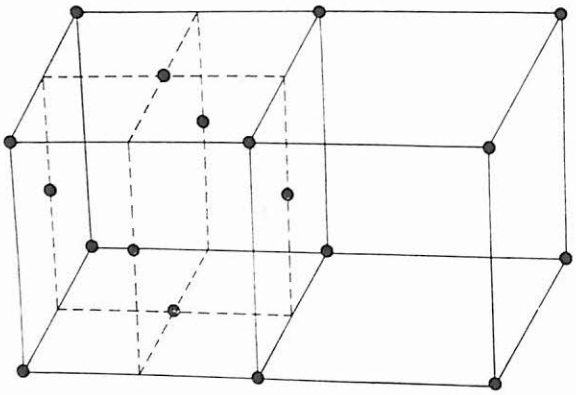


Fig. 9

If two body-centred cubes are drawn (*see* Fig. 10), the shaded (100) planes can be seen to be interleaved by planes exactly half-way between. There will therefore be no lines corresponding to (100) planes but, instead, to (200) planes; by the same argument there will be lines corresponding to (110) planes. The first line in a body-centred lattice must thus correspond to $h^2 + k^2 + l^2 = 2$. Similarly it can be seen for a face-centred lattice that reflections from both (100) and (110) planes will be absent and thus the first line will correspond to the (111) plane for which $h^2 + k^2 + l^2 = 3$. Possible values of $h^2 + k^2 + l^2$ for the three lattices are shown in Table VI.

A face-centred lattice is thus very easily recognized, and it will be seen that lithium, sodium and rubidium chlorides have this structure.

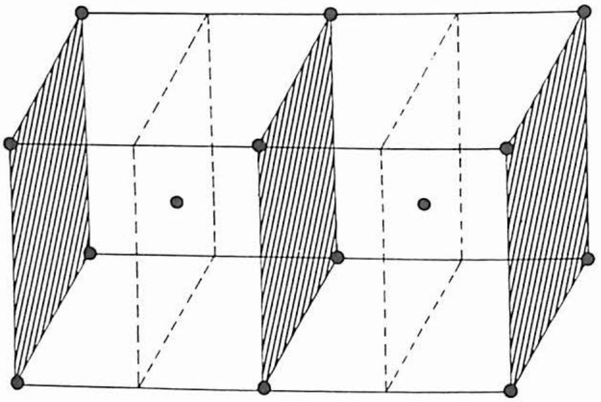


Fig. 10

It seems, too, that potassium and caesium chlorides have simple cubic lattices.

It is perhaps unexpected that there should be an apparent break in the series at potassium chloride. This will be looked at in more detail in the next article when I shall go on to arrive at the models of the five salts and to consider the nature of the structural units and of the bonds between them.

TABLE VI

Values of $h^2 + k^2 + l^2$

Simple cube	1	2	3	4	5	6	8	9	10	11	12	13	14	16	17	18	19	20
Body-centred		2		4		6	8		10		12		14	16		18		20
Face-centred			3	4			8			11	12			16			19	20

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CHEMICAL BONDS

III—IONIC LATTICES

By N. Booth, B.Sc.
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PROPERTIES OF THE ALKALI METALS

Before taking up again the examination of the powder photographs it may be useful to summarize the physical and chemical evidence which make it surprising that there should be any break in the series sodium, potassium, rubidium (*Educ. Chem.*, **1** (2), 67).

Sodium (2·6 per cent) and potassium (2·4 per cent) are about equally common in the earth's crust. In sea-water, however, there is much more sodium—about 1·1 per cent as against 0·04 per cent potassium. The two main reasons for this difference are that plants extract potassium and that potassium salts are in general less soluble than the corresponding sodium salts, so that some potassium salts are precipitated from the seas. Rubidium is very much less common in either land or sea.

All three elements are extracted by electrolysis of the molten chlorides, the equivalent conductivities at the melting point being shown in Table I.

TABLE I

Salt	Equivalent conductivity at melting point
NaCl	133·5
KCl	103·5
RbCl	78·2

Potassium itself is very similar to sodium but is more reactive, and rubidium still more so. Their electrode potentials and ionization potentials are shown in Table II.

TABLE II

Element	Electrode potential (V)	Ionization potential (eV)
Na	−2·71	5·14
K	−2·92	4·34
Rb	−2·99	4·18

All three metals burn with great vigour in oxygen, sodium to form a peroxide, potassium and rubidium to form superoxides.

Whilst sodium forms only monohalogen salts, potassium forms a tri-iodide which is only stable as the monohydrate and below 25°C; rubidium tri-iodide is anhydrous, crystalline and stable. Rubidium also forms a tribromide and mixed tri-halides.

The gradations of some other properties of the three metals and their compounds are shown in Table III.

TABLE III

	Na	K	Rb
Melting point	97·5°	63·4°	38·5°
Boiling point	889°	757°	701°
Melting point of chloride . .	800°	776°	715°
Heat of fusion of chloride ($cal\ g^{-1}$)	116	82	36
Heat of formation of chloride ($kcal\ mole^{-1}$)	98	104	105
Heat of formation of oxide ($kcal\ mole^{-1}$)	99	86	79

Evidently the chemical and physical properties of potassium are intermediate between those of sodium and rubidium. It would not do, however, to leave it at that, without emphasizing that although there is this gradation of properties, nonetheless the three are very similar indeed. The equivalent conductivities of the chlorides are all high, the electrode potentials very high, and the ionization potentials low. The melting points of the elements are very low compared with those of most metals, whereas the melting points of the chlorides are comparatively high. This is a genuine family of elements.

NATURE OF LATTICE PARTICLES

There are three possibilities to consider. Each lattice point could be occupied by an atom, a molecule or an ion. Thus, if the particles were molecules, each table-tennis ball in the face-centred models described earlier (*Educ. Chem.*, **1** (1), 20, Figs 8 and 9) would represent a molecule of the chlorides of lithium, sodium or rubidium except that, in order to account for the increasing value of the interplanar spacings as we go from lithium to rubidium, we should have to use larger balls for sodium chloride than for lithium chloride, and larger again for rubidium chloride.

There are other halides whose crystal structure can be worked out in exactly the same way as for the alkali-metal halides and which have very different physical and chemical properties. Iodoform, for example, has hexagonal symmetry, melts at 119°C, has a solubility of 0·01 g in 100 g water and 13·6 g in 100 g ether, both at 25°C, is not an electrolyte and does not give a precipitate with silver nitrate solution. Comparison with the properties of potassium chloride, which melts at 776°C, has a solubility of 27·6 g in 100 g water at 0°C, is insoluble in ether and is a good electrolyte (both molten and in aqueous solution), suggests that the lattice particles of iodoform are not of the same kind as those in potassium chloride. All the chemical evidence suggests molecules in iodoform but ions in potassium chloride.

The powder photographs confirm this; different intensities of the various lines provide the clues.

LINE INTENSITIES IN POWDER PHOTOGRAPHS

The powder photographs included in the previous article (*Educ. Chem.*, **1** (2), 67) show very clearly, especially in the case of sodium and rubidium chlorides, that some lines are strong, others weak. Now we might perhaps expect that the intensity of the scattered rays would be less for large angles of deviation and that the lines would become fainter as we moved further away from the right-hand spot, and we could certainly expect that the (111) lines would be very strong from a face-centred lattice because the (111) planes are those of closest packing (*Educ. Chem.*, **1** (1), 20, Figs 8 and 9); but, in fact, a visual estimate of the intensities of the lines in the sodium chloride photograph gives the result shown diagrammatically in Fig. 1.

Thus, all reflections from planes with *h*, *k* and *l* all even are strong lines whilst those from planes with *h*, *k* and *l* all odd are weak.

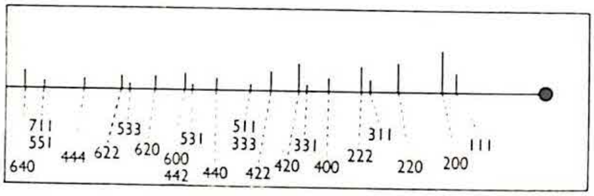

Fig. 1. Line intensities. Sodium chloride.

Let us now suppose that the sodium chloride crystals are made up of two different kinds of particles, which may be taken for the present to be either sodium atoms and chlorine atoms or the ions of the two elements, and that the lattice points are occupied alternately by sodium, chlorine, sodium, *etc.* Each kind of particle can then be arranged in a face-centred lattice, as the powder photographs show they must, and we shall now have two interpenetrating face-centred lattices as shown in Fig. 2.

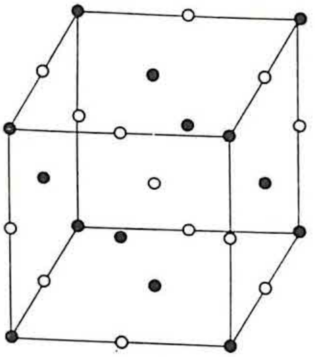

Fig. 2. Sodium chloride.

This model can now be checked to see whether it fits the evidence better than a model made up of only one kind of particle. Fig. 3 shows the (111) planes in the same lattice.

The sets of planes are very easily seen on a ball-and-stick model of the lattice, and, of course, the (111) planes are those seen before (Pt I, Figs 8 and 9).

Now if the reflections from all the (111) planes of sodium particles shown in Fig. 3 are in phase, those from the chlorine planes, which are exactly half-way between the sodium planes, will be exactly out of phase with them, and if the intensities of the reflected beams are equal there will be no (111) line on the powder photograph at all.

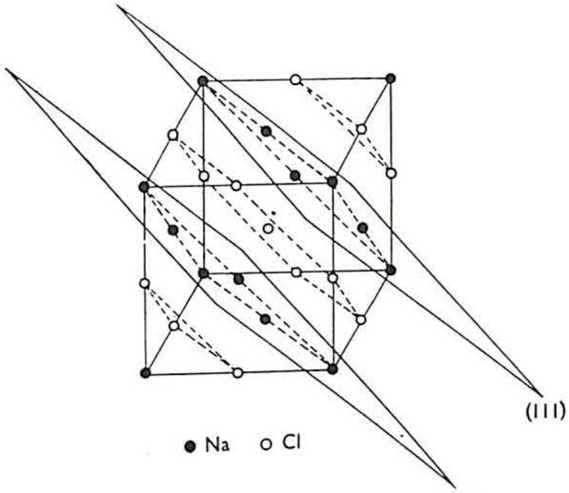

Fig. 3. Sodium chloride (111) planes.

But the (111) line, although strong, is not nearly as strong as several other lines, and certainly not as strong as would be expected if all the particles were identical. We can say then that the sodium chloride crystal is probably made up of two different particles which do not scatter X-rays with equal intensity. That all planes with indices all odd are interleaved by planes of different particles in the same way as the (111) planes can be seen from the two-dimensional lattice of Fig. 4.

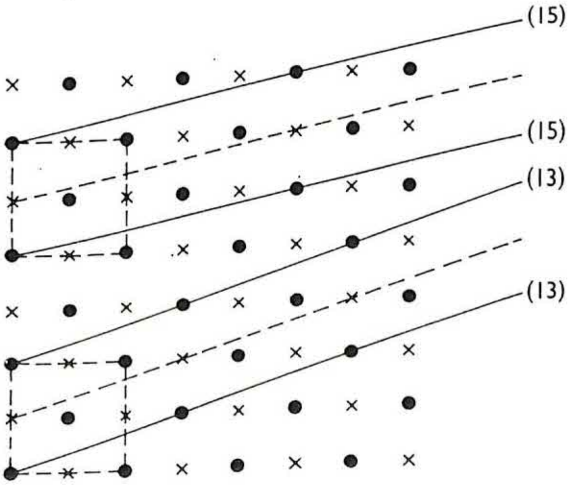

Fig. 4

On the other hand, as Fig. 5 shows, *all* the particles lie on the (200) planes, so that all can contribute to a strong reflected beam.

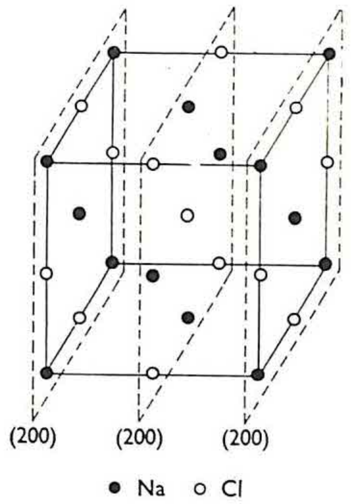

Fig. 5. Sodium chloride (200) planes.

A structure consisting of two interpenetrating face-centred lattices does account for the intensities of the lines in the sodium chloride photograph, and exactly the same applies to lithium and rubidium chlorides.

POTASSIUM CHLORIDE

It follows that if lithium, sodium and rubidium chloride crystals are lattices of metal particles and chlorine particles the same must be true of potassium chloride. It will have been noticed that in the photographs for lithium and rubidium chlorides the bright lines are not so bright, and the faint lines are not so faint, as the corresponding lines in sodium chloride. This suggests that, in the potassium chloride photograph, the faint lines may have disappeared entirely.

The lines for sodium and potassium chlorides are set out in Fig. 6, which shows that if the (*hkl*) values given for potassium chloride (Pt II, p. 72, Table II) are doubled, then potassium chloride would indeed fit into the series from lithium to rubidium.

But if the planes in potassium chloride for which (*hkl*) are all odd give no lines it can only mean that the reflections from a layer of potassium particles is completely cancelled by the reflections from the interleaved layer

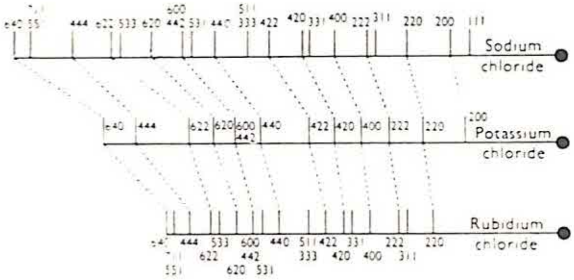

Fig. 6

of chlorine particles. That is, the scattering powers of the two particles are the same. Reference to Fig. 2 will show that if all the particles were identical the unit cell would be a simple cube, with an edge half the length of that of the actual unit cell.

This all fits into place if, in fact, the lattice points of all the crystals are occupied not by molecules or atoms, but by ions. A potassium ion and a chlorine ion each contain 18 electrons, and this equality may well account for the failure of X-rays to distinguish between them.

IONIC RADII

It has already been seen that the decreasing spacing of the lines in the photograph (Pt II, p. 67) is explicable in terms of increasing size of particle as we go from lithium to rubidium. If the lattices are ionic and the size of the chlorine ion remains constant this presumably means that the sizes of the metal ions are in the order $Li^+ < Na^+ < K^+ < Rb^+$.

Now that the crystal lattices of the chlorides of these four metals have been established, the interplanar distance can in each case be obtained from the density.

Reference to the sodium chloride lattice in Fig. 2 shows that in each unit cube there are:

Chlorine ions (○): One at the centre of the cube and belonging wholly to it; and one at the centre of each of the 12 edges, making 12 ions, each of which is shared between four unit cubes, so that the contribution of the 12 to the one cube is the equivalent of three ions. Thus there is the equivalent of four chlorine ions in the unit cube.

Sodium ions (●): Six at face-centres, each shared by two cubes, thus making the equivalent of a contribution of three ions to each cube; eight at the corners of the cube, each shared by eight cubes, making an equivalent of one to each separate cube. Thus there are four sodium ions to a cube.

Each unit cube then contains $4Na^+ + 4Cl^-$. Taking the density of sodium chloride as 2·18 g/cm³, the atomic weight of sodium as 23 and that of chlorine as 35·45, and the number of ions in a g-ion (Avogadro's Number) as $6{\cdot}02 \times 10^{23}$, the volume of the unit cube is given by

$$v = \frac{4 \times 58{\cdot}45}{2{\cdot}18 \times 6{\cdot}02 \times 10^{23}} \text{ cm}^3$$

$$= 1{\cdot}78 \times 10^{-22} \text{ cm}^3$$

Hence the side of the unit cube is:

$$a = 5{\cdot}64 \times 10^{-8} \text{ cm} = 5{\cdot}64 \text{ Å}$$

It may be noticed in passing that by combining the two expressions:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{and} \quad d = \frac{\lambda}{2 \sin \theta}$$

to give

$$\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}}$$

we can now calculate λ, the wavelength of the X-rays used. For example, for the (200) planes,

$$\lambda = a \sin \theta$$
$$= 5{\cdot}64 \sin 15{\cdot}75°$$
$$= 1{\cdot}53 \text{ Å}$$

Now the side of the unit cube, assuming a face-centred lattice, is twice the radius of a sodium ion plus twice the radius of a chlorine ion (*see* Fig. 5).

Thus $r_{Na+} + r_{Cl-} = 2{\cdot}82$ Å

Similar calculations give the shortest internuclear distance for each of the salts. In order to obtain from these values the radii of the ions of the various elements it is necessary to make theoretical estimates based on the number of electrons and the nuclear charge of the atoms. Thus, Pauling gives (*J. Amer. Chem. Soc.*, 1927, **49**, 765):

Ion	Radius (Å)
Li^+	0·60
Na^+	0·95
K^+	1·33
Rb^+	1·48
Cs^+	1·69
Cl^-	1·81

CAESIUM CHLORIDE

A caesium ion has 54 electrons, and therefore its simple cubic structure as indicated by the powder photographs cannot be accounted for in the same way as for potassium chloride. If, however, we consider a third method in which there are ions at the corners and the centre of the cube, this fits into place.

Fig. 7 shows one caesium ion at the centre of a cube, each corner of which is occupied by one-eighth of a chlorine ion. Such cubes stacked as shown in Fig. 8 would give a structure of two interpenetrating simple cubic lattices.

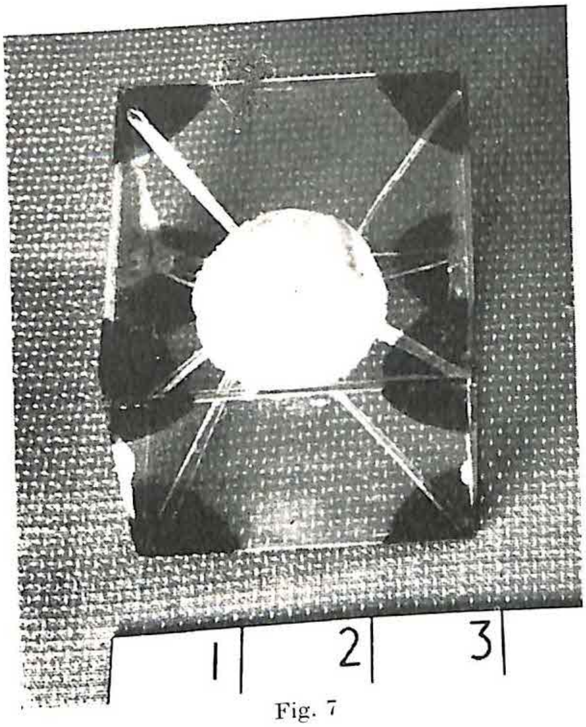

Fig. 7

It will be seen from Fig. 2 that in sodium chloride each chlorine ion is surrounded by six sodium ions as its nearest neighbours and similarly each sodium ion has six chlorines as nearest neighbours. In caesium chloride the number of nearest neighbours—known as the co-ordination number—is eight. This change must be related to the greater size of the caesium ion as compared with the other metal ions, *i.e.* the caesium ion can accommodate more chlorine ions around it.

The line intensities in the caesium chloride photograph are also of interest. The (100) line is weaker than might be expected and the (110), (211), (310), (321) and (411) (330) lines are stronger.

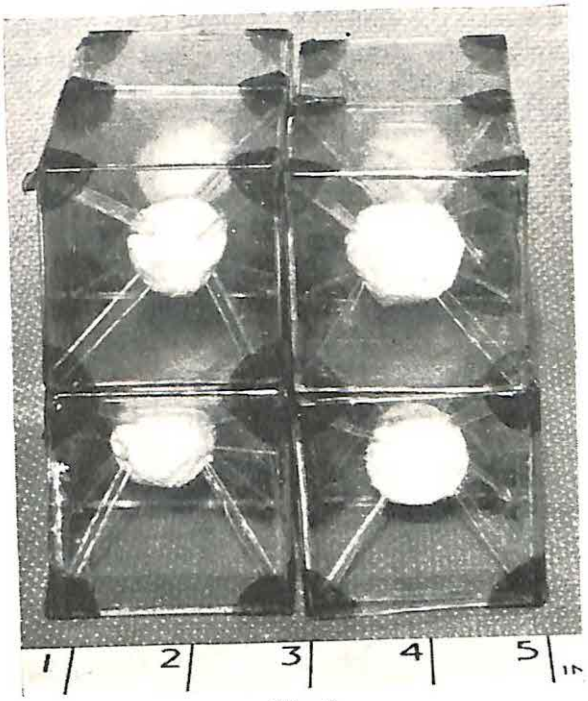

Fig. 8

Fig. 9 shows that the (100) planes are interleaved at exactly half the spacing by planes of ions of the opposite kind. As explained earlier, the result will be a weakening of the line resulting from reflections from these planes.

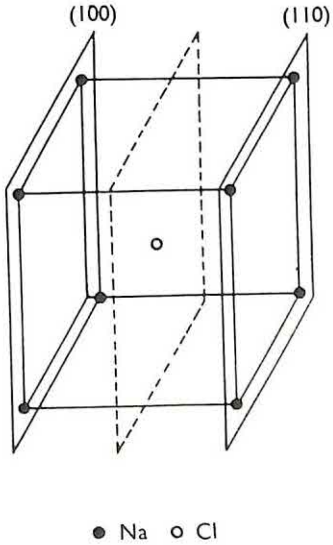

Fig. 9. (100) planes of caesium chloride.

Fig. 10, however, shows that all the ions lie in the (110) planes and so there is a very strong reflection from these planes. Further analysis in this way shows that for all planes for which the sum of *h*, *k* and *l* is even there should be a strong reflection, but for those for which the sum is odd there should be a weak reflection.

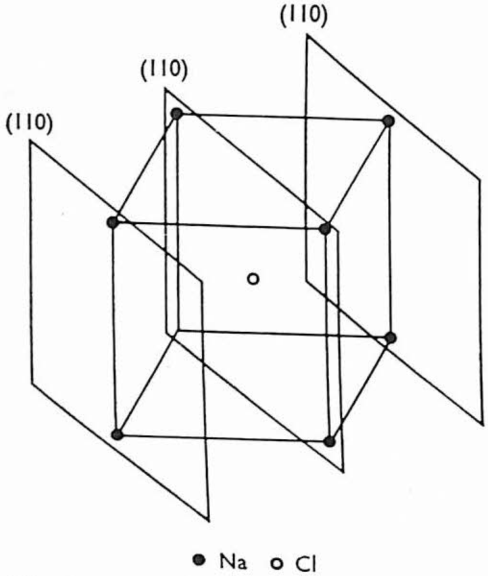

Fig. 10. (110) Planes of caesium chloride.

The (211) line is very much stronger than the (200) line, although the sum in both cases is even and the angle θ is greater for (211) than for (200). This introduces the last point about the photographs that will be dealt with. Clearly the intensity of the reflected beam from a set of planes will depend not only on the nature of the particles in the planes but also on the total number of planes—the more planes, the stronger the reflection. Now the three planes identified by (200), (020) and (002) will all reflect at the same angle, and there are only three such planes. Since in a powder there will be many crystals arranged at all possible angles to the incident beam of X-rays, each of these planes will give two reflections (*see* Fig. 11).

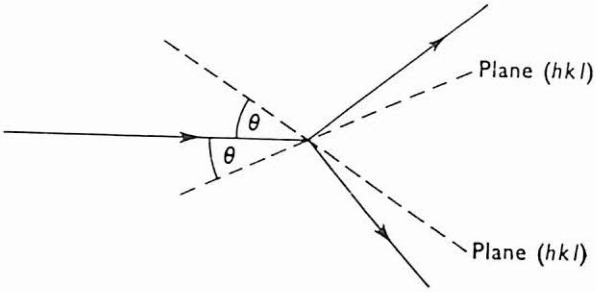

Fig. 11

Thus there are six orientations of the crystal which will result in reflections from these sets of planes. They may be represented by (200), (020), (002), $(\bar{2}00)$, $(0\bar{2}0)$ and $(00\bar{2})$.* But for the (211) planes there are 24 possible reflections, and this is why the line is so strong.

IONIC CRYSTALS

Most of the crystals met in the early stages of school chemistry are ionic. Their structures can be determined by similar methods to those applied here to the simple cubic crystals. In all of them the whole crystal is a single assembly of ions. Each ion is held in place by the electric fields of its nearest neighbours of opposite signs and also by the fields of the more distant ions of both signs. The ions therefore are held in place by strong forces, so that such crystals are usually hard and have high melting points.

The application of similar methods of analysis to crystals of the elements, compounds such as iodoform, and gaseous compounds will be dealt with in the next and final article.

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* If the rational planes have a negative intercept on the axes, the negative divisors, $-h$, $-k$, $-l$, are written $\bar{h}$, $\bar{k}$, $\bar{l}$ (cf. *Educ. Chem.*, 1964, **1** (2), 69).

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CHEMICAL BONDS

IV—METALS, NON-METALS AND NON-IONIC COMPOUNDS

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METALS

Analysis of the X-ray photographs of the metals, that is of those elements which comprise groups IA, IB and IIA, together with the transition elements, shows that, with few exceptions, they all have one of the three structures: (*a*) face-centred cubic, *e.g.* copper and silver; (*b*) body-centred cubic, *e.g.* sodium and potassium; or (*c*) close-packed hexagonal, *e.g.* magnesium.

The face-centred cubic and the hexagonal lattices can be shown to be the result of closest packing of spheres. We have seen (*Educ. Chem.*, 1964, **1**(1), 18) that close-packed layers consist of hexagons made up of six spheres packed around a central sphere of the same size.

The two methods of close packing in three dimensions can be demonstrated by making three hexagons, each numbered like that shown in Fig. 1. Polystyrene spheres held together by lengths of pipecleaner and a cold-water glue are very convenient for this purpose. One of the hexagons is laid on a flat surface—call this layer A—and the second hexagon is placed above it, but slightly displaced so that its sphere 1 is in the gap formed by spheres 1, 3 and 4 of layer A. We now have layer B above layer A. Sphere 1 of the third hexagon is now placed in the gap formed by spheres 1, 5 and 6 of layer B so that layer C is above layer B. If two extra spheres are added—one to layer A beside spheres 2 and 3, one to layer B beside spheres 7 and 2—it will be seen that these additional spheres, together with 1, 2, 3, 4 and 7 of layer A, 1, 2, 3 and 7 of layer B, and sphere 2 of layer C, form an incomplete face-centred cube. The cube would be completed by placing a fourth hexagon under layer A and directly below layer C.

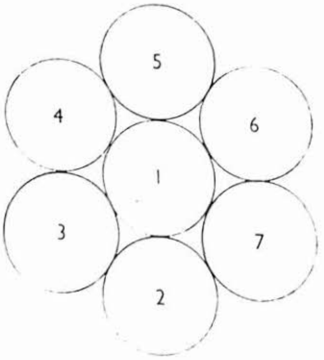

Fig. 1. Closest packing of equal spheres

If, however, layers A and B are laid down exactly as before, but layer C is immediately above layer A, *i.e.* layer C is set so that its sphere 1 is in the gap between spheres 1, 6 and 7 of layer B, we have hexagonal close-packing. The two arrangements can then be represented thus:

face-centred cubic—A,B,C; A,B,C; . . .
hexagonal close packing—A,B; A,B; . . .

Examination of both lattices constructed in this way will show that each sphere is in contact with 12 others. In fact, sphere 1 of layer B is in contact in the face-centred lattice with the following: spheres 1, 3 and 4 in layer A; spheres 2, 3, 4, 5, 6 and 7 in layer B; spheres 1, 2 and 3 in layer C. In both these structures the co-ordination number is 12. In a body-centred cubic structure, however, the co-ordination number is 8, that is to say, the packing is not so tight.

When teaching the subject in schools the correlation of many of the physical properties of metals and alloys with the established structures could be discussed at this point, and the 'metallic bond' be introduced.

NON-METALS

The structures of most of those non-metals which are solid at ordinary temperatures have been elucidated by X-ray analysis, but only carbon will be dealt with here. In the form of diamond, carbon was one of the first crystals to be investigated by W. H. Bragg and W. L. Bragg.

Analysis by powder photographs, in exactly the same way as previously described for the alkali-metal halides (*Educ. Chem.*, 1964, **1**(2), 71), shows that diamond also belongs to the cubic system and further that it has a lattice of two interpenetrating face-centred cubes. The lines A-A in Fig. 2 are drawn to indicate planes formed by atoms at the corners of the smaller cubes. Lines B-B indicate planes formed by atoms at the centres of smaller cubes. If a face-centred unit cube is divided into eight small cubes and a carbon atom placed at the centre of alternate small cubes, the diamond lattice is given. It can be built up from the units shown in Fig. 3, the small cubes being constructed from cellulose-acetate sheet, and the whole and part spheres being of expanded polystyrene.

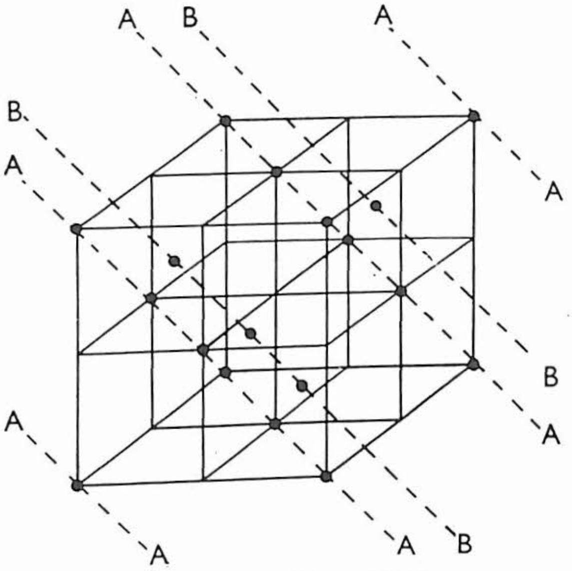

Fig. 2. Unit of diamond lattice

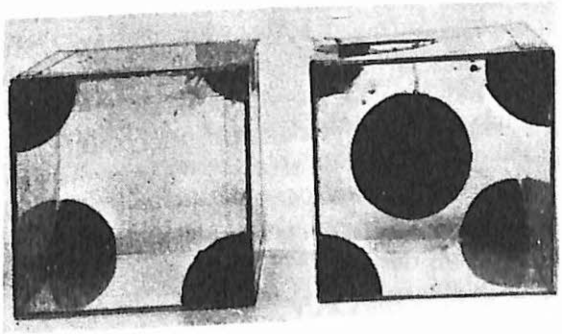

Fig. 3

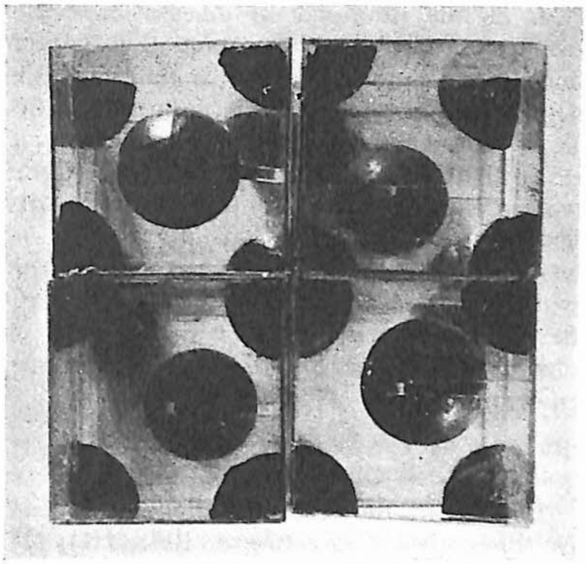

Fig. 4.

Fig. 4 shows the assembled lattice from which it can be seen that each carbon atom is surrounded by four other carbon atoms situated at the corners of a regular tetrahedron. It should be noted that in reality the atoms are most probably in contact or almost so. They are separated in this model only so that their arrangement can be seen. Fig. 5 shows 12 of the smaller cubes assembled and demonstrates that the lattice is face-centred. Exactly similar calculations to those used in the previous examples in this series (*Educ. Chem.*, 1964, **1**(3), 154) give the separation of the atom centres as 1·54Å. This gives an atomic radius for carbon of 0·77Å. Silicon and germanium are found to have structures similar to that of diamond—a giant molecule of atoms bound together tetrahedrally.

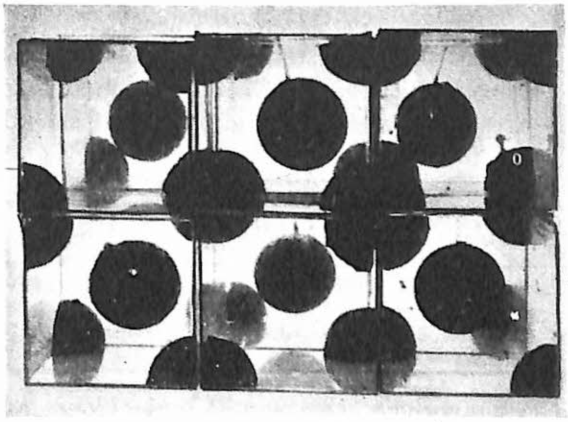

Fig. 5

It is not proposed to discuss here the nature of the bond between the carbon atoms in diamond except to underline the significance of the co-ordination number of 4. It is never found necessary to postulate a co-ordination number greater than 4 for carbon, although the number is frequently less, no matter with what other atom or atoms it is combined. Thus, the factor which limits the number of atoms that may be accommodated around a carbon atom is not, as was the case with ionic compounds, the relative sizes of the atoms.

SIMPLE MOLECULES

The board described in the first article in this series (*Educ. Chem.*, 1964, **1**(1), 21) may be used again as a simple introduction to this topic. In this case additional holes are drilled in the board at 2-cm intervals along the centre line and three combs are used, one originating from each of the two vertical arms and the third from the central horizontal line.

If we refer to these combs as A for upper vertical, B for lower vertical and C for horizontal and use them in pairs we have the following possible coincidences: AC, BC, AB. Putting A in the seventh hole, B in the seventh hole and C in the second hole, the results given in Table I are obtained; the distances to the point of coincidence are measured as the perpendicular distance from the point of coincidence to the centre line.

TABLE I

Distance (cm)	3·5	7·5	10·5	13·5	0
Combination	AB AC	AB BC AC	AB AC	AB BC AC	AB BC AC

When this is repeated for A = 5, B = 5, and C = 4, the results given in Table II are obtained. Fig. 6 shows how these can be represented diagrammatically. The pattern obtained depends, as to position and intensity of lines, on the arrangement of the points of origin of the three combs. This again is the principle of the method of determining the shapes of gaseous molecules with X-rays. A beam of X-rays falling on a molecule will be scattered by the atoms which compose it; each atom acts as a point of origin of secondary X-rays in the same way as the selected holes on the board act as points of origin for the combs. The positions of the maxima and minima, recorded on a photographic plate, will allow us to calculate the positions of the atoms, provided the wavelength of the X-rays is known.

TABLE II

Distance (cm)	4·8	9·3	12·8	14·0	0
Combination	AB BC AC	AB	AC BC	AB	AB

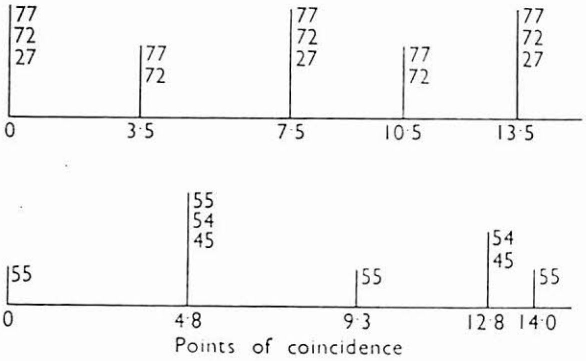

Fig. 6

It should be noted that, as it stands, the above is only strictly correct if we have a single molecule motionless in space. Real experiments have, however, to be carried out with a very large number of molecules, each of which has three possible modes of motion: translation, rotation and vibration. In addition, the atoms are not points but have a diameter comparable to the wavelength of the X-rays used, and the combined effect of all these factors is to reduce the variations of intensity on the photographic plate, but not, however, to make them disappear entirely.

In general it is found that the greater the atomic weight of an atom the more effective it is in scattering X-rays although it would be more accurate to say that the intensity of scattering depends on the average electronic density.

One of the first molecules to be investigated by X-rays was carbon tetrachloride by

P. Debye in 1930, a very appropriate molecule to use since it contains four atoms of fairly high atomic weight, and there was already ample evidence that its structure was tetrahedral with a Cl–Cl distance of 2·99 Å. It was therefore possible to calculate a theoretical distribution of the X-ray diffraction pattern and also of the intensities of the various expected maxima, and to compare the calculations with the results obtained by experiment. Agreement within one per cent was obtained. As was expected, when chlorine atoms were replaced by hydrogen atoms to give successively $CHCl_3$, CH_2Cl_2 and CH_3Cl, the maxima became less distinct but it could nevertheless be shown that the Cl–Cl distance increased slightly with decreasing number of chlorine atoms. The result of all this was to confirm the tetrahedral structure and strongly to suggest that the bond angles increase slightly as more chlorine atoms are introduced, as though these atoms were repelling each other.

This early work on carbon tetrachloride is typical of most investigations of molecular structure by X-rays. Most organic molecules, for example, are complex structures by comparison with the inorganic salts, and X-ray analysis has generally been used to provide the final check on information gained by chemical methods of analysis. Thus, for example, X-ray analysis has shown that benzene is a flat, regular hexagon with all six hydrogen atoms in the plane of the hexagon and with each CCH angle 120°.

The most dramatic use of X-rays is in the unravelling of the structures of the molecules found in living creatures, with the result that it is becoming clear that beneath the great variety of living forms lies a relatively small number of molecules which undergo similar chemical changes in organisms as diverse as a virus and a mammal. The problems posed by such complicated structures as protein molecules can only be fully resolved by X-ray analysis.

CONCLUSION

An attempt has been made in these four articles to show how it is possible in schools to give a simple and yet reasonably thorough and valid introduction to what might justly be described as the most fruitful scientific weapon of the 20th century.

Analysis of X-ray photographs of the simpler structures is well within the grasp of pupils in the sixth forms of our schools, and a qualitative interpretation possible before this. It would be helpful if a small booklet was produced containing X-ray photographs ranging from powder photographs of the simpler ionic compounds to those of one or two biochemical structures.

ACKNOWLEDGMENT

I am greatly indebted to Dr S. C. Wallwork of Nottingham University for his encouragement and guidance in the early stages of planning this series of articles, and for the practical help he gave in making it possible for me to obtain the powder photographs shown in Part II. Also, to Mr H. F. Halliwell of Keele University and the Nuffield Foundation, without whose initial enthusiasm it is unlikely that the articles would have been written.

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Crystal Structure Analysis for Undergraduates

In the University of London, experimental and theoretical courses in structural crystallography are given at two levels. There are various day and evening graduate courses intended for specialists, two of which are complete two-year intercollegiate courses covering every aspect of modern crystallography. One of these, based on Birkbeck College, has a physical-chemical slant; the other, at the Battersea College of Technology, a metallurgical bias.

The various component Colleges of the University also teach chemical crystallography to their chemistry undergraduates, but usually only in the form of lecture courses. At University College, however, the undergraduates themselves asked for a practical course; and the following article gives an account of such a 25-hour course which has now run annually for over ten years. The aim of the exercise is to make chemistry students appreciate the fundamental theory basic to diffraction analyses of atomic or molecular crystal structures, to realize the potentialities of various techniques and to form a personal judgment of their accuracy; it also gives students the chance of handling crystallographic equipment.

Preliminary Lecture Course

The practical course is preceded by a few lectures in which the structures of simple atomic and ionic crystals are described systematically and their chemical relevance discussed; the Bragg relation is derived and applied to the various types of diffraction pattern; and the use of diffraction techniques (X-ray, electron, neutron) for identification and chemical analysis is demonstrated by examples. The students are also taught the elements of symmetry, space-group theory, and nomenclature (*4a*), and are shown how the diffraction spectra are dependent upon the distribution of scattering matter. They learn how the simplest types of structure are deduced:

when there are no variable parameters. (All atoms are in special positions.)

when there is only one variable parameter (or a few).

when the attainment of a preliminary structure, suitable for refinement by computer, depends upon the use of modern techniques of phase determination.

The Experiments

Usually the students work in pairs, 3 or 4 pairs being in the laboratory at any time and each student spending 5 hours a day for five consecutive days on the practical course. The whole class is first shown all the equipment in the laboratory, including some that they will not actually use (such as a crystal-sphere-grinding apparatus, low-temperature and multiple-exposure photogoniometers, Geiger-counter diffractometers, apparatus for measuring magnetic susceptibilities, etc.) and are told something of the various research problems in progress. They are shown an X-ray tube in pieces and are given special instructions about safety precautions and the importance of avoiding X-ray exposure of any part of the body and especially the fingers. The apparatus is, of course, made as foolproof and accident-proof as possible, but it is nevertheless regarded as very important that students should know what precautions have been taken and the reasons for each of them.

The problems undertaken, in alternate years, are the determination of the structures of urea and hexamethylene tetramine. The students begin with the crystals (dimensions about 0.5 mm each way) and end with a Fourier electron-density map from which the stereochemistry can be seen at a glance and the interatomic distances and angles measured with an accuracy of about 5%. In the case of (tetragonal) urea, half the class determine the projection along the *c* axis [001], the other half that along the *a* axis [100], so that by comparing notes they have the full geometry of the structure (see Figs. 6, 7). In the case of hexamethylene tetramine, $C_6N_4H_{12}$, all the class determine a cube-axis projection (see Fig. 9).

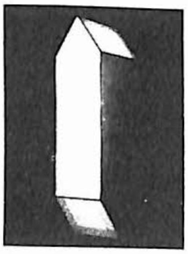
Figure 1. Cardboard model showing idealized shape of urea crystal, symmetry $\bar{4}2m$.

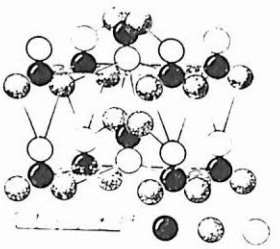
Figure 2. Ball-and-spoke model of urea crystal structure. The long spokes indicate the outline of one unit cell and the general directions of the NH · · · O bonds.

Urea, $CO(NH_2)_2$ is water soluble and crystallizes in space-group $P\bar{4}2_1m$. Crystals, a cardboard model of an "ideal crystal" (Fig. 1), and a ball-and-spoke model of the crystal structure (Fig. 2) are provided for examination of the geometrical relationships between them. The students carry out the following experiments, not necessarily in the order given (since they must use certain of the apparatus by turn) but always in a logical order.

Observations using a polarizing microscope.
Measurement of single-crystal density, by flotation.
Measurement of interfacial angles using an optical goniometer.
Determination of the size and shape of the unit cell and the

number of molecules of $CO(NH_2)_2$ in it (Laue and rotation X-ray photographs).

Comparison of a powder photograph with the spot positions and intensities on a rotation photograph and indexing of the powder lines.

Indexing of zero-layer-line spots on the rotation photograph and estimation of their intensities. Reduction of data to give "structure factors" ($\{hk0\}$ or $\{h0l\}$).

Optical synthesis of the observed structure factors, using phase data provided (scale 1 cm = 1 Å).

Measurement of interatomic and intermolecular distances and observation of the general shape of the molecules in relation to their packing.

Urea is uniaxial, with straight extinction when mounted with the prism length (the *c* axis) parallel to the microscope stage. It is seen that if one of the pyramid faces is taken as (111) then the prism faces are {110}, and a rough measurement of either of the angles $(111):(\bar{1}\bar{1}1)$ or $(111):(110)$ can be used to give an approximate value of the axial ratio c/a, to be compared later with the more accurate determination by optical or X-ray goniometer measurements. Students realize that quite simple polarizing-microscope measurements may sometimes be used for nondestructive determinative chemical identification.

Density by Flotation. The students select small single crystals, if possible without inclusions or bubbles, and use liquids respectively less and more dense than the specimen, and in which they are not soluble, as components of the flotation mixture. The advisability of accepting the maximum density as correct (since bubbles tend to decrease the density) and the necessity of measuring and recording the ambient temperature are pointed out. For more exact methods, students are referred to the appropriate section of Volume III of "International Tables for X-ray Crystallography" (*4c*).

The use of density as a check on identification of a very small quantity of material and for purposes of molecular weight determination is indicated.

Optical Goniometer. This instrument provides a means of measuring interfacial angles, the accuracy of which is dependent upon the perfection of the faces; in many cases, it can permit easy nondestructive identification of well-crystallized materials. It also familiarizes students with the use of goniometric crystal holders by means of which centering and orientation can be controlled, and a modified form of which they will meet subsequently on the X-ray photogoniometer. It does help them to see visually, by means of microscope and telescope attachments, what will later be happening to the X-ray incident and diffracted beams as the crystal is adjusted on its sliders and arcs.

Laue Photograph. The mounting of a film or of a pack of films in a cylindrical camera will be new to students and should be practiced first with old films in the light.

Two Laue photographs have to be taken with either the (001) axis vertical and [110], [1$\bar{1}$0] in turn along the incident beam or a [100] vertical and [010], [001] in turn along the beam. The crystal setting is made using a small microscope fitted on to the photogoniometer and will not usually be more than approximate. The final adjustment to bring [001] or [100] exactly vertical is made from the X-ray photographs since the crystal photograph should be symmetrical about a horizontal line. The original setting of a face (110) parallel to an arc of the goniometer head and then normal to the incident beam, which has to be done by eye, is not critical. The final adjustment of the crystal on the arcs, which must be done after measurements of the photographs and calculations from them, must be exact if good rotation photographs, suitable for intensity measurement, are to be obtained. The calculation for adjustment is simple and a good student should not need to be told the necessary formula but may have to be warned to choose a pair of spots above and below the equator which are as near as possible to the vertical plane through the incident beam and the arc parallel to it.

The similarity of the two Laue photographs both taken with (001) vertical and at right angles to each other, proves the existence of the fourfold symmetry axis. The presence of diffuse streaks and spots, as well as sharp Laue spots, even on a 15-min photograph (Fig. 3) is evidence of thermal vibrations of large amplitude.

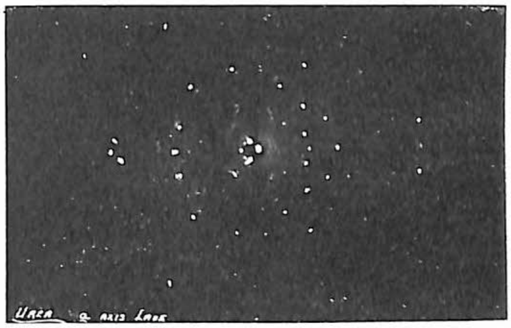

Figure 3. Laue photograph of urea single crystal, taken with white radiation containing a CuK characteristic component, which is responsible for the diffuse streaks, these being due to molecular vibrations. The [001] is vertical; the [100] is nearly along the incident beam. Exposure time, 15 min.

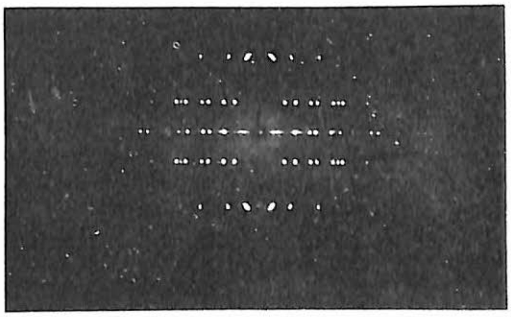

Figure 4. Rotation photograph of urea, [001] vertical, showing layer lines *hk*2, *hk*1, *hk*0, *hk*$\bar{1}$, *hk*$\bar{2}$. Cu$K\alpha$ (filtered Ni).

Rotation Photograph. Once the crystal has been accurately set, [001] or [100] vertical, the taking of a rotation photograph is simply a matter of inserting a Ni filter to eliminate Cu$K\beta$ (and some continuous) radiation, releasing the crystal spindle, and of exposing to the Cu$K\alpha$ incident beam for about 30 min (Fig. 4).

The films are processed at a standard temperature in a thermostatted darkroom, and the critical effect of temperature on the chemical reactions involved in photographic processing is pointed out. So also is the (differential) effect of humidity on the dimensions of the film after processing and at the time of measurement. This is more critical than temperature and is often overlooked even by experienced research workers. It is one of the main reasons why standard marks on the film are required in precision work.

The following sets of measurement are made on the processed film when it is dry:

Averaged distances y_n between pairs of layer lines n and $\bar{n}$: hence a calculation of the repeat (identity) distance c or a (Å).

Distances x between pairs of similar spots along the equatorial layer-line; hence a calculation of the Bragg angles θ and the spacings d (Å).

Intensities I (averaged for each pair) of the equatorial layer-line spots, by eye estimation using a comparison intensity scale which is provided (*2*).

The Table of d and I entered into the laboratory notebooks should contain a column into which the indices $hk0$ or $h0l$ will be subsequently entered.

Powder Photograph. A few small crystals are ground very finely using an agate mortar and pestle. Mixed with a little cellulose acetate, the powder can easily be rolled into a cylinder of size about 1- × $^1/_4$- × $^1/_4$ mm³. This specimen is then centered on the camera spindle, with its cylinder axis vertical, and a Ni filter inserted for the exposure. It is educationally helpful to use not a "strip," but a full cylindrical film for the powder photograph (Fig. 5) so that the latter can be superimposed on the well-set (or mis-set) rotation photographs and the positions of lines and spots compared and so that the effects of preferred orientation can be understood even if they are not actually observed.

The appearance of a strip can of course be shown by masking, and the special features of a normal "strip" powder camera demonstrated. The intensities of powder lines and rotation spots should also be compared and the necessity of a correction for multiplicity on powder photographs will be appreciated by reference to an offset rotation photograph.

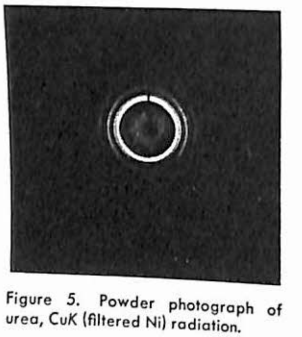
Figure 5. Powder photograph of urea, CuK (filtered Ni) radiation.

Determination of Unit-cell Size and of the Number of Molecules in the Unit Cell. Since urea is tetragonal, $a = b \neq c$, $\alpha = \beta = \gamma = 90°$. This may be demonstrated by orthogonal Laue photographs and by optical goniometric measurements.

Students working with the prism axis [001] as rotation axis will have determined c from layer-line separations. They determine a from the $d(hk0)$ values measured from the equatorial layer-line spots. It is found that odd orders of $h00$ are absent. This is evidence of two-fold screw axes (2_1) parallel to [100] and [010]. The indices $hk0$ of all spots on the zero layer line are easily determined. The *row* lines connecting $hk0$, $hk1$, $hk\bar{1}$, $hk2$, etc. on successive layer lines are easily recognized and this facilitates the indexing of all the hkl reflections.

The value for a ($=b$) has been determined from layer-line separations. The value for c is determined from the $d(0kl)$ values measured on the equatorial layer line.

The reflections on the 1st, 2nd, etc., layer lines will be $1kl$, $2kl$, etc., and can usually be identified by inspection, as above. The difference in certain multiplicities for rotation and powder reflections may be pointed out.

When all the hkl spots on the rotation photograph have been identified, superposition of the powder photograph will identify the powder lines; and intensities can be visually compared. The powder line intensities are then listed as *VS, S, MS, M, MW, W, VW*. The use of charts and other independent means of identifying indices of lines on powder photographs generally can be mentioned, but in this short course there is no time to attempt these in practice. References to suitable books (see Bibliography) are of course given, and the use of powder photography in the "fingerprint method" of chemical identification, using the ASTM index, or a direct comparison method, is again emphasised. This is probably the principal future use of X-ray techniques as far as the majority of chemists are concerned.

Given a, c, and the density ρ, the number n of $CO(NH_2)_2$ molecules in the unit cell is derived from

$$a^2c\rho = nM/N$$

where M is the molecular weight and $N = 6.024 \times 10^{23}$.

Optical Synthesis of Structure. The "structure factor" F (on a relative scale) for each reflection can be obtained from the observed intensity I as follows:

$$I = F^2 \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot P \cdot \text{constant}$$

where the unknown constant is independent of angle apart from an absorption factor which is negligible except for more refined structure analyses. The angle factor, which allows for the polarization of the X-ray beam and the period of reflection time of each plane, is obtained from tables to which the students are referred (*3*). P is the multiplicity, with which they should have become thoroughly familiar.

Each F value represents a scattered wave in a particular direction, of an amplitude dependent upon the distribution of scattering matter relative to the set of (hkl) planes giving the spot in question. It can be represented, as a sine function, by a set of optical fringes of suitable contours. An optical reconstruction of the projected crystal structure can be made by superposing, photographically, on a single sheet of film or paper, as many sine waves as there are reflections observed on the equatorial layer line (($hk0$) for an [001] projection (Fig. 6); ($0kl$) for a [100] projection (Fig. 7)). These fringes must have the correct relative *spacings* (wavelength proportional to $d(hkl)$), *orientations* (corresponding with the relative orientations of the reflecting planes), *amplitudes* (exposure times proportional to F) and *phases*. The phases are supplied. They cannot be directly observed by the student and are obtained in this case by calculation from a trial structure; the student does not have time in this course to carry out these calculations. He may do so as an exercise on some other occasion.

There are various devices available for making such optical Fourier syntheses, for example, by means of

Huggins' masks, Lipson's X-ray microscope, or the von Eller photosommateur. We use the latter *(1)* in which the origin of the sine wave is a line source of light passing through a specially-designed diffraction grating. This is movable on an optical bench, to and fro (for adjustment of spacing) or from side to side (for adjustment of phase). The photographic paper is in a cassette capable of rotation normal to the optical bench length and carrying with it a mounting to which can be fastened a "reciprocal net," made by the student on a scale that will give a final reproduction in which 1 cm ≡ 1 Å. This can be found by trial before the course begins, together with a suitable *total* exposure time, the latter being fairly critical if a good picture is to be obtained.

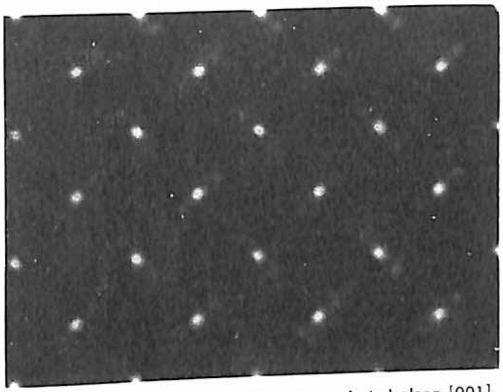
Figure 6. Optical synthesis of urea structure, projected along [001].

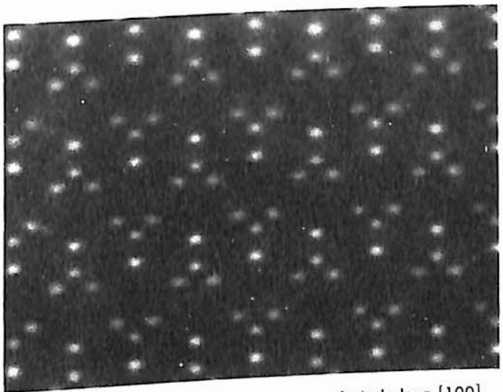
Figure 7. Optical synthesis of urea structure, projected along [100].

The students who have obtained the (001) and the (100) projections (Figs. 6 and 7) should now compare them with each other and with the model (Fig. 2) of the structure as a whole. They can even directly measure, from their photographs, projected C=O and C—N intramolecular distances and NH····O intermolecular distances, and can calculate the actual distances; or they can determine the atomic coordinates from the photographs and hence calculate the bond lengths. These may be compared with similar bond lengths in other compounds by reference to Tables 4.2 (Tables of Bond Lengths between Carbon and other elements) in Vol. III, "International Tables for X-Ray Crystallography." This will give the students some idea of the meaning (and accuracy of measurement) of bond lengths in relation to chemical constitution.

Hexamethylene tetramine, $C_6N_4H_{12}$, is very soluble in water, slightly soluble in alcohol and is best crystallized from a weakly aqueous alcohol solution. The crystals are cubic, space group $I\bar{4}3m$.

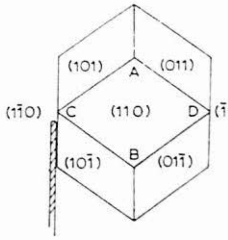

Figure 8. Diagrammatic representation of hexamethylene tetramine crystal, as mounted on glass fiber for Laue or rotation photograph.

The experimental procedure is rather similar to that for urea, except that all the class determine a cube-axis projection (Fig. 9) by setting their crystals with the short diagonal of a (110) face vertical. This is AB in Figure 8, which shows the habit, having twelve similar {110} faces. It would be quite useful if one-half of the class were to set CD vertical, thus obtaining a (110) projection. This, however, is a little more difficult to visualize in relation to the cubic symmetry.

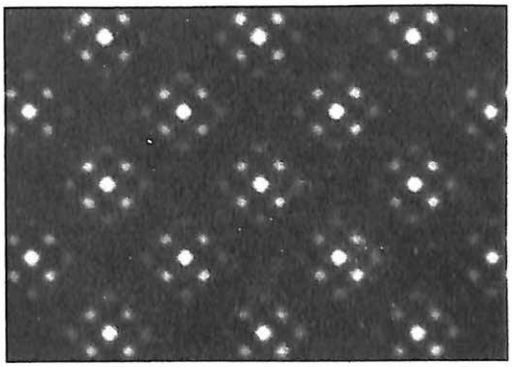
Figure 9. Optical synthesis of hexamethylene tetramine structure, projected along [100].

Since hexamine is isotropic, it is advisable, when making observations with a polarizing microscope, to give the students a few crystals of urea so that the optical behaviour of the two substances may be compared and contrasted. The c/a axial ratio for urea may also be measured. For hexamine it is checked that the angles CAD or CBD, which are $109\frac{1}{2}°$, can be measured with an accuracy of about 1 in 200 by lining up each face edge in turn with a crosswire (this assumes that a graduated microscope stage is available). Crystals of dimensions about $\frac{1}{2}$- × $\frac{1}{2}$- × $\frac{1}{2}$ mm^3 should be selected for X-ray work and of about twice this size (linear) for optical goniometry. A few good small crystals without visible inclusions or internal bubbles are also selected for density measurement.

The procedure is then very similar to that for urea, except for the following points:

Since hexamine is frequently rather "perfect," the crystals used for X-ray work need to be first dipped in a little liquid N_2 (or liquid air) in a watchglass, in order to make their texture more "mosaic." Theory and experiment have shown that the intensity of reflection from a perfect crystal, which shows strong "extinction" due to multiple internal reflection and other causes which attenuate the primary beam, may be several times less than that from a mosaic crystal. Students may be shown X-ray photographs illustrating the "before" and "after" effects of this sudden thermal shock. Even urea diffraction intensities may sometimes be improved by similar thermal treatment.

Since for any cubic crystal $1/d^2 = (h^2 + k^2 + l^2)\ a^2 = (4\sin^2\theta)\ \lambda^2$, it follows that the values of $\sin^2\theta$ deduced from a powder photograph of a cubic crystal will be found to be proportional to all or some of the possible values of $(h^2 + k^2 + l^2)$ where h, k, and l are integers. This enables the diffracting planes to be indexed (hkl), the lattice type to be identified and the value of the lattice constant a to be determined, given λ.

All three cubic lattices are readily identifiable from the first three reflections of a misset rotation photograph since the multiplicities observed will be

$\{hkl\}$	100	110	111	200	210	211	220	300	310
P	(6	12	8)	6	24	24	12	6	24
I	...	(12	...	6	...	24)	12	...	24
F	...	...	(8	6	...	...	12)	...	...

General multiplicities for the $\bar{4}3m$ class of the cubic system are

$\{h00\}$	$\{hh0\}$	$\{hhh\}$	$\{hk0\}$	$\{hhl\}$	$\{hkl\}$
6	12	8	24	24	48

The differences between the lattices are due to the following conditions:

P all hkl reflections may be observed.

I only hkl where $h+k+l$ is even are present, all others have zero intensity.

F only hkl where h, k, l are all even or all odd are present; all those with mixed indices are of zero intensity.

The students note that for cubic crystals a second kind of multiplicity may occur where h, k, l may be two or more different sets of integers for the same value of $h^2+k^2+l^2$. Thus $h^2 + k^2 + l^2 = 18$ will correspond to both $\{330\}$ and $\{411\}$. These would coincide on powder or on [110] rotation photographs, but would be differentiated on a Weissenberg (moving film) photograph about [110] or on a [100] rotation photograph.

The main result achieved by this exercise, apart from those already mentioned for urea, is the realization of the very high symmetry of the $C_6N_4H_{12}$ molecule (Fig. 9). The equality of all the carbon atoms cannot be brought out by the formula as printed even in a structural form. It can only be seen in a spatial representation. The C—N distances as measured from the optical projection may be compared with those found for urea, and as recorded for other compounds containing this bond. The significance of the body-centered arrangement of these nearly spherical molecules in relation to intermolecular bonding should be pointed out in contrast with adamantane, $C_{10}H_{16}$, which is face-centered cubic.

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Section 4 Stereochemistry

F. A. Cotton, in the introduction to his paper on "Ligand Field Theory", states that the presentation of this theory in a first college chemistry course cannot be said to be essential. Nevertheless, this theory has had such a profound effect on inorganic chemical research in particular that all chemistry teachers should have at least some acquaintance with it. This article is the best available introduction for any chemist not yet familiar with the theory.

The article by E. L. Eliel, gives the content of two lectures on the principles of stereochemistry to first-year college students with little knowledge of organic chemistry the aim being to make the student realize why a reaction may be stereo-selective or stereospecific. This approach, which contrasts with those in which great emphasis is placed on optical rotation, is justified by the fact that most of the major components of living matter are disymmetric and are so generated in biochemical syntheses.

The last decade has seen a great advance in our understanding of the three-dimensional structure of organic molecules. H. L. Allinger's paper suggests the content of a two or three-hour lecture introduction to conformational analysis which could greatly stimulate the student's interest in organic chemistry. Further ideas on presenting the subject will be found in G. Baddeley's paper which indicates the type of evidence on which our ideas concerning stereochemistry are based.

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Ligand Field Theory

The presentation of ligand field theory in the first college chemistry course cannot be said to be essential. If time is limited, or if the ability of the students and/or their interest in chemistry as a pure science rather than as a branch of useful knowledge are not well above average, I believe there are many other topics which can be more profitably discussed. There is time enough in later years of the chemistry curriculum for those who do elect chemistry as a major subject to tackle this aspect of it. However, in a thorough sort of course, taught to a select, science-oriented group of students, the subject of ligand field theory might form an interesting and stimulating part. Certainly it is an important part of the "vocabulary" of modern theory which teachers should know so that their presentation not be erroneously simplified at any level. It is important, however, to present it in such a way as to avoid creating false impressions about the nature of ligand-to-metal bonds; this requires of the teacher, first, an awareness and understanding of the dangers and, second, the possession of some concrete ideas about how to avoid them. This article presents an outline of ligand field theory in its present state and at an introductory level; it suggests, partly in precept and partly in example, a presentation of this subject which is primarily intended to be appropriate in the general chemistry course, but it also raises some points which will be of concern to those introducing ligand field theory to students at any level.

Ligand field theory can be defined as the theory of (1) the origins and (2) the consequences of the splitting of inner orbitals of ions by their surroundings in chemical compounds. In this article we shall restrict attention primarily to penultimate *d* orbitals, i.e., the 3*d* orbitals for ions of the first transition series, 4*d* and 5*d* orbitals for ions of the second and third transition series. To a considerable degree, it is possible to deal with the two parts of ligand field theory separately; this has the important consequence that many of the significant and relatively straightforward results of *d*-orbital splittings, e.g., ligand field stabilization energies, stereochemical preferences and, of course, spectroscopic and magnetic behavior, can be discussed pragmatically without necessarily going very far into the inherently difficult and tedious question of what causes the splittings. Of course, a truly *rigorous* discussion of *all* the consequences of inner orbital splittings could not be given without intimately interweaving an examination of the causes, but for most undergraduate courses—and certainly for the introductory course—such rigor and comprehensiveness are unnecessary.

Causes of Inner Orbital Spittings

The possibility that the degeneracy of atomic orbitals will be significantly split when an ion is placed in a chemical environment was first suggested by Becquerel (*1*) and the problem was then examined in considerable detail by Bethe (*2*). Bethe's work consists of two parts: first, in one of the earliest applications of symmetry arguments to a chemical problem, Bethe determined the qualitative nature of the orbital splittings for various important geometries. These qualitative results are correct whatever the mechanism (electrostatic, or covalent, as discussed presently) which brings them about. For *d* orbitals, in several important geometrical situations, they are as follows:

> In both octahedral and tetrahedral surroundings, the d_{xy}, d_{xz}, and d_{yz} orbitals remain equivalent, as do $d_{x^2-y^2}$ and d_{z^2} orbitals.
>
> In square surroundings, the d_{xz} and d_{yz} orbitals remain equivalent, but the d_{xy}, $d_{x^2-y^2}$ and d_{z^2} orbitals are not equivalent to any others.

Bethe obtained these and other results by formal, group-theoretical methods, but they can also be obtained, or at least their correctness strongly suggested, by informal, pictorial arguments, requiring only the common sense[1] any bright freshman should have. To do so, it is first necessary to present pictures showing the shapes of the usual five d orbitals, Figure 1. In addition, it should be pointed out that the d_{z^2} orbital can be regarded as a combination, in equal parts, of two orbitals, $d_{z^2-x^2}$ and $d_{z^2-y^2}$, each of which is shaped like the other four d orbitals; this is illustrated in Figure 2.[2] It is now supposed that the metal ion is placed in an octahedral array of six ligands, as shown in Figure 3.

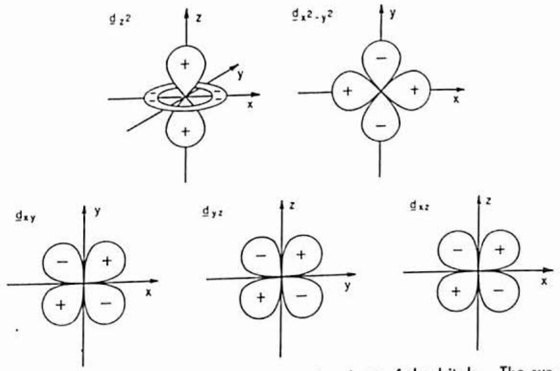

Figure 1. Balloon pictures of the conventional set of d orbitals. The surfaces are drawn to enclose a major part—say, roughly, 90%—of the amplitude of the wave functions. The sign of the wave functions in each lobe is shown. Since the distribution of electron density is given by ψ^2, it will in each case be quite similar to the shape of the wave functions of the orbitals.

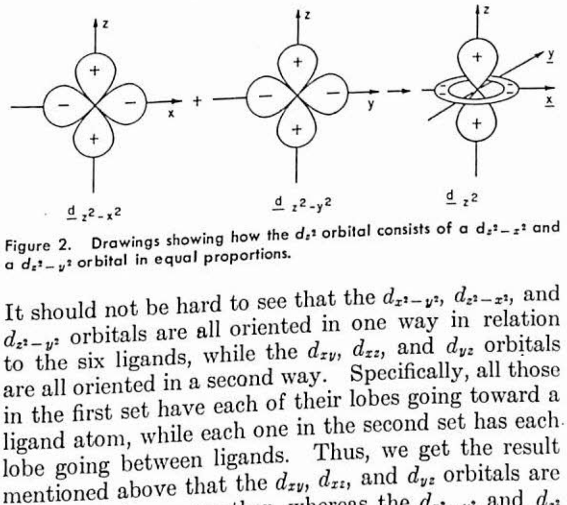

Figure 2. Drawings showing how the d_{z^2} orbital consists of a $d_{z^2-x^2}$ and a $d_{z^2-y^2}$ orbital in equal proportions.

It should not be hard to see that the $d_{x^2-y^2}$, $d_{z^2-x^2}$, and $d_{z^2-y^2}$ orbitals are all oriented in one way in relation to the six ligands, while the d_{xy}, d_{xz}, and d_{yz} orbitals are all oriented in a second way. Specifically, all those in the first set have each of their lobes going toward a ligand atom, while each one in the second set has each lobe going between ligands. Thus, we get the result mentioned above that the d_{xy}, d_{xz}, and d_{yz} orbitals are equivalent to one another, whereas the $d_{x^2-y^2}$ and d_{z^2} (being made up of equal parts of the equivalent pair $d_{z^2-x^2}$, $d_{z^2-y^2}$) are different from the first three, but equivalent to one another.

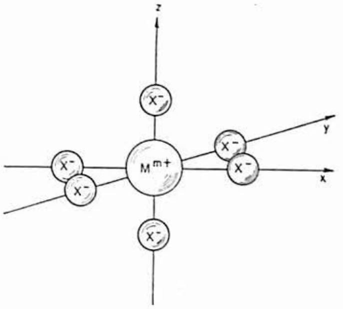

Figure 3. The arrangement of the six ligand atoms in an octahedral complex in relation to the same Cartesian coordinate system used in Figures 1 and 2 for the d orbitals.

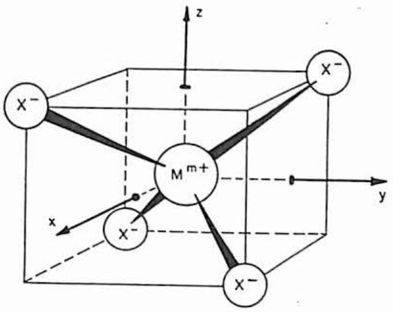

Figure 4. The arrangement of the four ligand atoms in a tetrhaedral complex in relation to the same Cartesian coordinate system used in Figures 1 and 2. Note how the tetrahedron is composed of four alternate corners of a cube.

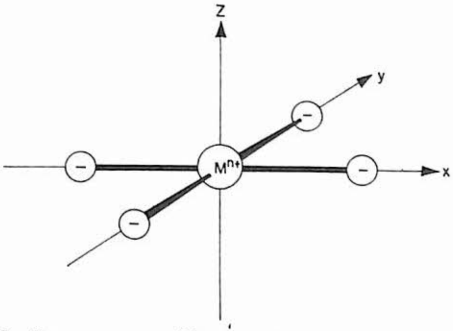

Figure 5. The arrangement of four ligand atoms in a square complex in relation to the same Cartesian coordinate system used in Figures 1 and 2.

Similarly, for a tetrahedral set of four ligands, arranged as shown in Figure 4 at alternate vertices of a cube,[3] it can be seen that the d_{xy}, d_{xz}, and d_{yz} orbitals stand in one sort of relationship to the ligands, namely, with their lobes pointing to cube edges, while the $d_{x^2-y^2}$, $d_{z^2-x^2}$, and $d_{z^2-y^2}$ orbitals stand in another relationship; namely, their lobes point to the centers of cube faces. Hence, again, we conclude that d_{xy}, d_{xz}, d_{yz} form one equivalent set while $d_{x^2-y^2}$ and d_{z^2} form a second equivalent set.

Finally, it can be seen that the d_{xz} and d_{yz} orbitals both have the same relationship to the ligands set at the corners of a square in Figure 5, that both $d_{z^2-x^2}$ and

---

[1] Someone is supposed to have remarked that "group theory is just organized common sense," which is not too great an exaggeration.

[2] For algebraic details, see Cotton and Wilkinson, page 973. It is necessary to make this breakdown of the d_{z^2} orbital in order to demonstrate by the pictorial argument that d_{z^2} and $d_{x^2-y^2}$ are not only different from the other three, but also are *equivalent to one another*. It is to be stressed, however, that the $d_{z^2-x^2}$ and $d_{z^2-y^2}$ orbitals have no *actual* existence along with the other four, since there can be only *five* independent nd wave functions.

[3] The usefulness of this way of looking at a tetrahedron, for many purposes besides the present one, is worth emphasizing.

$d_{x^2-y^2}$ have a second relationship to the ligands and that each of the two remaining orbitals is related in still different ways.

The question now arises as to how much the energies of the nonequivalent orbitals, or sets of orbitals, may differ. It must be assumed that if two orbitals, even if intrinsically similar, are differently oriented toward their surroundings, there will, in principle, be some difference in the energy of an electron depending on which of them it occupies.

The second part of Bethe's paper offered an answer to this question based on the assumption that the ligands can be treated as *point* negative charges, a model which has often been considered to represent the chemist's concept of purely ionic bonding. (In fact, it does not, as will be seen.) Using this model, it is easy to see that qualitatively, an electron in an orbital whose lobes point at the negatively charged ligands will have a higher electrostatic potential energy than an electron in an orbital whose lobes point between ligands. In other words, the former orbital is a less stable one and lies higher on an energy level diagram of the usual type than does the latter orbital. Figure 6 illustrates these results for the octahedral, tetrahedral and planar cases. It should be noted that for the square environment, the ordering of the orbitals is not exactly fixed by the symmetry alone, but depends in certain respects (e.g., as to whether the d_{z^2} orbital lies above or below the d_{xy} orbital) on the physical details. The arrangement shown in Figure 6 is the one believed to be correct in most real cases. More generally, the relative stabilities of a series of inherently similar orbitals will vary inversely according to the extent to which they bring the electron into proximity with the negative ligands. The argument may be generalized to include not only negatively charged ligands, but dipolar ones, which will be so oriented as to have their negative ends closer than their positive ends to the metal ion. Bethe showed further that the actual magnitudes of the energy differences (e.g., Δ_0 and Δ_t in Figure 6) can be calculated using this electrostatic model if one can select the proper magnitudes for the metal-ligand distance, and the ligand charge (or dipole moment) and assign an appropriate radial part[4] to the wave function for the *d* orbitals. In relatively recent times, Ballhausen (*3*) showed that if these parameters are assumed to have the same values in an octahedral complex, MX_6 and a corresponding tetrahedral one, MX_4, the ratio of Δ_t to Δ_0 will be $^4/_9$. It has also been shown that the absolute values of Δ_0 (or Δ_t) can be obtained within a factor of less than two by choosing reasonable values for the various parameters required.

However, in spite of all this sort of pragmatic success, this electrostatic model is now known to be unrealistic and ultimately unsatisfactory. It has been discredited both experimentally and theoretically. The experimental evidence against it comes from a variety of sources all showing that electrons which are supposed to be entirely in the metal ion *d* orbitals, according to Bethe's point charge model, actually spend a part of their existence in orbitals "belonging" to the ligand atoms.[5] Such results imply that there is covalence in the metal-ligand bonding; some of the data permit quantitative estimation of the amount of covalence.

From the theoretical side, the inadequacy of the point charge model (as other than a physically meaningless formalism leading to useful equations) may be described as follows (*4*). First, let us recognize that the ligand atom is *not* a point. It is an object of about the same size as the metal ion and it is built in the same way. An F^- ion, for example, consists of a positive nucleus of charge $+9e$, which *is essentially a point*, surrounded by a spherical cloud of total charge $-10e$, about 90% of which lies within a sphere whose radius is about equal to half the M—F distance in an MF_n complex ion or in a MF_n salt.

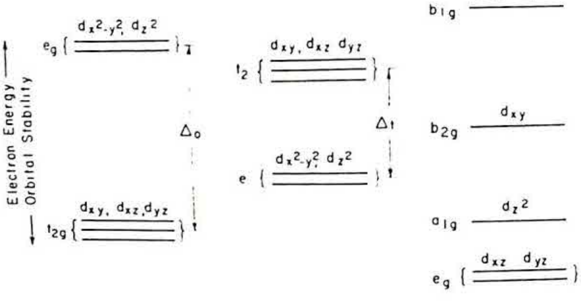

Figure 6. Orbital splitting diagrams for the three most important types of complex. Orbitals within each pair of braces are of identical stability.

The point charge model does not meaningfully correspond to the concept of ionic bonding because a point charge does *not* meaningfully represent the way one ion "looks" to the outer electrons on another ion which is within about two Å of it.[6] However, a reasonable representation of a purely electrostatic interaction between the *d* electrons of a cation and an anion, is that given in Figure 7, where the anion is shown as an entity with structure and finite size, as described above. Using this qualitatively realistic representation of the physical situation, the following argument may be developed.

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[4] When an orbital wave function is expressed in spherical coordinates $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$, the radial part is the $R(r)$. The parameter r measures the radial distance from the origin. The angular part of the wave function is $\Theta(\theta)\Phi(\phi)$ which involves the direction in space from the origin and depends only upon the angles θ and ϕ

[5] The evidence will not be reviewed here. Several summaries are cited in the bibliography. Those in ORGEL, BALLHAUSEN, and COTTON AND WILKINSON are especially recommended.

[6] To more deeply buried electrons of a cation, a near neighbor anion may come closer to appearing as a point negative charge. Recall in this connection a basic theorem of electrostatics, due to Gauss, which states that if a test charge lies completely outside of any charged sphere, it experiences the same force as it would if all the charge on or in the sphere were concentrated in a point at the center of the sphere. For the rare earth ions, calculations of orbital splittings using the point charge model may therefore have somewhat more physical meaning, although there is evidence (*5*) to show that here, too, covalence plays a role. The one important situation that comes to mind in which the point dipole model for the surroundings of a cation may be physically realistic is in the computation of the electrostatic effect produced by an array of ions in a crystal which lie outside of the first coordination shell of the cation being treated. Even for second nearest neighbors, however, some significant covalence effect, or orbital overlap, evidently occurs as shown by the existence of a contact shift (*6*) in the nuclear resonance frequency of ^{17}O in the ion pair or "outer sphere complex."

An electron occupying an orbital which has lobes such as A and A′ in Figure 7, directed at the ligand atoms will feel the positive charge of the nucleus (or the net positive charge of the compact core, in a heavier atom) rather strongly, thus off-setting appreciably the repulsive effect it feels from the diffuse electron cloud into which it penetrates. On the other hand, an electron occupying an orbital which has lobes, such as B and B′ in Figure 7, directed between ligand atoms feels the repulsive effect of the electron cloud nearly as much as the electron in A, but feels the countervailing effect of the nucleus less. Thus, instead of concluding that the electron must be much more stable in orbital B than in A, as we do in the point charge model, we conclude that the stability difference will be either only slightly in favor of B, or possibly, even *slightly in favor of orbital A*. Actual calculations, using realistic (i.e., Hartree-Fock) orbitals for metal and ligand atoms have shown this to be true quantitatively (*4*). Thus, if we take a realistic model of the ligand and consider only electrostatic metal-ligand interactions (that is, assume a model which *realistically* represents "ionic bonding") we cannot explain the observed splittings of *d* orbitals.

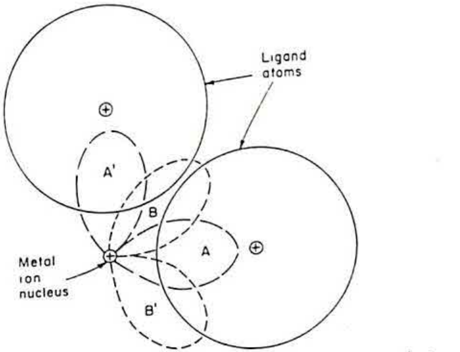

Figure 7. A drawing of part of a complex showing two lobes, A, A′ of an e_g type metal orbital, two lobes, B, B′ of a t_{2g} type metal orbital and two ligand atoms. The spheres enclosing most of the electron clouds of the ligand atoms are also shown.

It has been shown, however, that when the effects of covalent bonding are introduced, they give a splitting which is qualitatively correct and, if sufficiently elaborate calculations are made (*very* elaborate, unfortunately), almost quantitatively correct results can be obtained (*7*).

It is not very difficult to see, at least qualitatively, that covalent bonding will operate in this way. When each of two atoms has an orbital directed toward the other one (σ_1, σ_2, Fig. 8*a*), and these atoms approach to within a few Angstroms of one another, the orbitals become mixed to form two new orbitals, one, (σ_B), having relatively high amplitude (high electron concentration) between the two nuclei and the other, (σ_A), having relatively low amplitude (low electron concentration) between the nuclei. When electrons occupy the first, (a bonding orbital), the atoms become bound together, while when electrons occupy the second, (an antibonding orbital) a repulsive or antibonding force is set up. Furthermore, if the two atomic orbitals with which we begin have rather different energies, the resulting bonding orbital will have predominantly the characteristics of the lower energy atomic orbital, while the resulting antibonding orbital will have predominantly the characteristics of the higher energy atomic orbital: this is represented in Figure 8*b*. However, if the two atomic orbitals (π, σ in Fig. 9) are of such a nature that they have no *net* overlap, there is no mixing and no formation of bonding and antibonding orbitals.

Now the relationship shown in Figure 8 is that between the e_g orbitals[7] of a metal ion and the σ orbitals of ligand atoms, while the relationship shown in Figure 9 is that between the t_{2g} orbitals of a metal ion and the σ orbitals of ligand atoms. The complete result, a combination and elaboration of Figures 8*b* and 9*b* is shown in Figure 10.

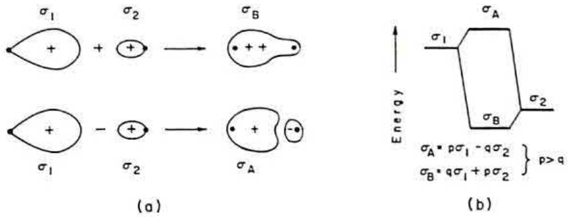
σ_1
σ_2
σ_B
σ_A
Energy
$\sigma_A = p\sigma_1 - q\sigma_2$
$\sigma_B = q\sigma_1 + p\sigma_2$
p > q
(a)
(b)

Figure 8. Sketch showing the formation of bonding and antibonding π type orbitals, such as those formed by overlap of metal e_g orbitals with appropriate ligand orbitals in octahedral complexes.

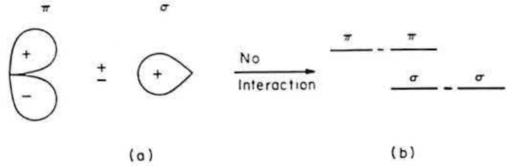

Figure 9. Sketch showing the lack of interaction between a σ orbital (such as a t_{2g} orbital of a metal ion) and a ligand σ orbital.

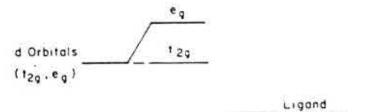

Figure 10. Energy level diagram showing the results of all the interactions between the σ orbitals of a ligand and the t_{2g} and e_g orbitals of a metal ion.

Now it can be seen that by considering the overlap of orbitals, we have arrived at the same qualitative result as that given by the point charge electrostatic model: the fivefold degeneracy of the *d* orbitals is split in an octahedral environment, so that the e_g orbitals become less stable than the t_{2g} orbitals. For all of the principal chemical consequences of orbital splittings, if is only necessary to know the correct ordering of the orbitals; the actual magnitude of the splitting, Δ_0 or Δ_t, can be left as a parameter to be determined in some one experiment and the results of other experiments then predicted. Thus, while the point charge model is physically without meaning, it does give results which are in general qualitatively correct. It can therefore be considered as a useful *mathematical* model, but it should not be taught as in any sense a *physical* model.

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[7] The symbolism here adopted is that now most generally accepted. Readers need not worry about its full implications which derive from the use of Mullikan symbols and character tables to describe molecular symmetry. The *e* implies a two-dimensional representation, *t*, a three-dimensional representation; *g* (from the German *gerade*, meaning even) implies even symmetry with respect to inversion. (See Cotton, F. A., "Chemical Applications of Group Theory," p. 72.)

Some Consequences of Inner Orbital Splittings

When the degeneracy of a set of orbitals is split, electrons no longer will occupy all members of the set with equal probability. Instead, they tend to occupy the more stable ones preferentially, subject to restrictions arising from Pauli's exclusion principle and from interelectronic repulsions. The former require no special discussion; they are the same as for free atoms and ions. For present purposes, the phenomenon of interelectronic repulsion—which results from both simple coulombic repulsion and from exchange energy variations—can be expressed as follows: the placing of a second electron in an orbital already occupied by one electron, instead of in an equivalent, but unoccupied orbital, requires the expenditure of an interelectronic repulsion energy, or pairing energy, P, which, to a reasonable approximation, may be considered a constant for all of the nd orbitals of a given ion. With only these simple considerations, it is possible to forecast accurately the way, or the two possible ways, in which the electrons will be distributed amongst the d orbitals of an ion in an octahedral ligand field for any case from d^1 to d^9. Similar arguments can be devised for cases where the ligands are differently arranged, e.g., tetrahedrally, or in a square.

For a d^1 ion, the single electron naturally goes into one of the t_{2g} orbitals, and the ion can be said to have a t_{2g} configuration. Similarly, d^2 and d^3 ions will have t_{2g}^2 and t_{2g}^3 configurations, with each electron in a different t_{2g} orbital and all electron spins parallel (Hund's rule[8]), as shown in Figure 11*a*. For a d^4 ion, there are two possibilities. All electrons may occupy the t_{2g} orbitals (t_{2g}^4) but then one orbital must be doubly occupied and the stability of the configuration is lessened by the pairing energy, P. Alternatively, we may have the configuration $t_{2g}^3e_g$ which does not require expenditure of pairing energy, but does require expenditure of the energy Δ to elevate one of the electrons to the unstable e orbital. The configuration which is actually adopted in a given case is determined by which of these energies is the smaller: if $\Delta < P$ we have $t_{2g}^3e_g$ and if $\Delta > P$ we have t_{2g}^4. The $t_{2g}^3e_g$ configuration has four unpaired electron spins, while t_{2g}^4 has only two unpaired electron spins. Accordingly, the former is called the *high-spin* configuration and the latter the *low-spin* configuration.

For a d^5 ion we may have the high-spin $t_{2g}^3e_g^2$ configuration, in which the total energy expended to put electrons in e_g orbitals, rather than t_{2g} orbitals, is 2Δ or the low-spin configuration t_{2g}^5 in which the energy $2P$ is expended to pair up electrons. Again, the criterion which determines the preferred arrangement is simply whether P or Δ is the smaller quantity. These results, as well as those obtained analogously for the d^6 and d^7 cases are illustrated in Figure 11.

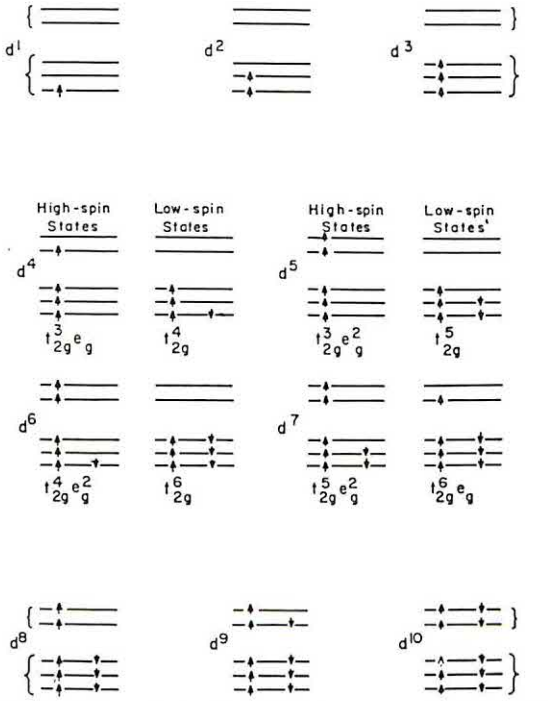

Figure 11. Diagrams showing the most stable arrangements of electrons in the *d* orbitals of ions in octahedral complexes.

For a d^8 ion, it is impossible to have fewer than three electron pairs, and the configuration having the greatest number of t_{2g} electrons, $t_{2g}^6e_g^2$, must be the most stable. Similarly, for a d^9 ion, the most stable arrangement must be $t_{2g}^6e_g^3$. By exactly similar arguments, the results for tetrahedral complexes can be obtained. (Note, by reference to Figure 6, that in this case, the e_g orbitals are lower in energy than the t_{2g} orbitals.) However, so far as is known at present—and few if any exceptions are ever likely to be discovered—there are no low-spin tetrahedral complexes. This is because tetrahedral splittings Δ_t are too small to exceed P. Therefore, the only important results for the various d^n ions in tetrahedral complexes are the following high-spin configurations:

$d^1:e^1$ $d^4:e^2t_2^2$ $d^7:e^4t_2^3$
$d^2:e^2$ $d^5:e^2t_2^3$ $d^8:e^4t_2^4$
$d^3:e^2t_2^1$ $d^6:e^3t_2^3$ $d^9:e^4t_2^5$

The purely theoretical possibility of a low-spin configuration does exist, however, for the d^3–d^6 cases.

It is to be noted that these results were obtained without any knowledge of the actual cause of the splitting or any specification of the energies of the t_2 and e orbitals relative to any reference energy whatever. With these configurations as a basis, it is possible now to examine some of the important consequences of the d orbital splitting.

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[8] Hund's rule, originally established from spectroscopic studies, states that the lowest of several possible energy states for a free atom or ion will be that with "maximum multiplicity." The multiplicity is defined as $2S+1$ where $S = \Sigma s_i$, the spin vectors of the electrons occupying the equivalent orbitals. In effect, it means that electrons spread out over a set of equivalent orbitals with their spins parallel to the maximum possible extent. See, for example, HERZBERG, G., "Atomic Spectra and Atomic Structure," Prentice-Hall, Inc., New York, 1937, p. 135.

Magnetic Properties

In order to predict or explain magnetic properties of a transition metal ion in its complexes or other compounds, our first need is always to know how many unpaired electron spins it has or may have. The discussion may then proceed to higher levels of sophistication if desired, but this basic question of how many unpaired electrons there are must always be answered first.

By referring to the electron configuration diagrams in Figure 11, we see first of all that for d^1, d^2, d^3, d^8, and d^9 ions in octahedral environments, there will always be 1, 2, 3, 2, or 1 unpaired electrons, respectively, no matter how great the value of Δ_0 may become.[9] Deviations from these numbers in the d^2, d^3 or d^8 cases (provided it is certain they are not due to any intermolecular effects) can be taken to indicate that the environment of the ion actually departs appreciably from the octahedral arrangement.

For d^4, d^5, d^6, and d^7 ions, the number of unpaired electrons can be either the high-spin ones, 4,5,4,3 respectively, or the low-spin ones, 2, 1, 0, 1 respectively, depending on the magnitude of Δ_0 relative to P for the ion in question. Now the value of P for a given ion can be evaluated fairly reliably from data on the spectrum of the gaseous ion; P values are, with few exceptions, known quantities. Therefore, for a series of complexes of a given ion, some high-spin and some low-spin, we can draw the conclusion that all ligands giving the low-spin configuration produce Δ values in excess of P, while all ligands giving the high-spin configuration, produce Δ values less than P. From the spectrum of an ion in a given complex, the actual value of Δ can be determined (see below). It has been found, without exception, that predictions of the kind just described are correct. For instance, for the d^6 configuration of Co^{3+}, data from spectra of the gaseous ion lead to a value of about 50 kcal/mole for the pairing energy. For $[CoF_6]^{3-}$, the Δ_0 value is only about 37 kcal/mole, while in $[CO(NH_3)_6]^{3+}$ Δ_0 is about 66 kcal/mole. In agreement with these facts, $[CoF_6]^{3-}$ has four unpaired electrons, while $[Co(NH_3)_6]^{3+}$ has none. For the d^6 configuration in the Fe^{2+} ion, the pairing energy is about 40 kcal/mole, while the Δ_0 value in $[Fe(NH_3)_6]^{2+}$ is only about 35 kcal/mole. Therefore $[Fe(NH_3)_6]^{2+}$ unlike $[Co(NH_3)_6]^{3+}$ should have the high-spin configuration with four unpaired electrons, and it does.

Ligand Field Stabilization Energies

The fact that for most of the d^n configurations the electrons do not occupy all five orbitals with equal probability, but instead tend to occupy three of them in preference to the other two in an octahedral field (or two in preference to the other three in a tetrahedral one) has both energetic and structural consequences. Some of these are sufficiently straightforward that they can probably be incorporated into an introductory treatment. Others, however, such as Jahn-Teller effects,[10] are probably best omitted. In the following paragraphs, the sort of coverage which might be given to a few thermochemical topics is outlined; some structural ones will be similarly discussed in the following part of this section.

The derivation of ligand field stabilization energies has usually been given with implicit (or explicit) reference to the idea that the e_g orbitals lie $^3/_5\Delta$ above and the t_{2g} orbitals $^2/_5\Delta$ below the energy which all the d orbitals would have if they were surrounded by the same total electrostatic charge but not split—which would happen if the charge were uniformly distributed over a sphere instead of concentrated into six equal amounts at the vertices of the octahderon. This raising and lowering of the energy of the sets of orbitals by amounts inversely proportional to their degeneracies is a manifestation of the general rule of the "preservation of the center of gravity." It is a rigorous result in the point charge model, but *not* in a more general form of ligand field theory in which the orbital splittings are ascribed to covalent interactions. It is therefore important to derive all results pertaining to ligand field stabilization energies by an argument which does not in any way use a "center of gravity rule," although the argument which does so gives correct results. For example, in a complex where the ligands have little or no interaction with the t_{2g} orbitals, the splitting arises mainly or entirely from an upward shift of the e_g orbits (see Fig. 10). A discussion of ligand field stabilization energies (LFSE's) which uses only the fact that the energy of the e_g orbitals is higher by Δ_0 than that of the t_{2g} orbitals in an octahedral complex may proceed as follows.

For an entire transition series of ions, of given charge, e.g., Ca^{2+}, (Sc^{2+}), Ti^{2+}, V^{2+}, . . . Ni^{2+}, Cu^{2+}, Zn^{2+} (Sc^{2+} is in parentheses because it has not actually been obtained in an ordinary chemical compound) we expect a fairly smooth variation of the bond energies from the d^0 to the d^{10} ion for the complexes or compounds with a particular ligand or anion. This is because we expect a fairly smooth variation in the energy of each type of orbital and hence of the overall energy of formation, provided all the orbitals are either equally occupied in each case or the population increases uniformly. Now for all the orbitals except the d orbitals, the populations are constant throughout such a series. For the d orbitals, the *total* population increases steadily, but in the ligand field, there are two different sets of d orbitals (or d-like orbitals) whose separate populations do *not* increase uniformly. The e_g population goes from 0 to 4 and if the increase were uniform, there would be a change of $^4/_{10} = {}^2/_5$ electron at each step. Similarly, a uniform increase in the population of the t_{2g} orbitals would mean an increase of $^6/_{10} = {}^3/_5$ electron at each step. On this basis, the figures for the "uniform" e_g and t_{2g} populations shown in Table 1 are obtained. Below them are the actual populations, as indicated in Figure 11, for the high-spin states. It is clear that for the d^0, d^5, and d^{10} cases the "uniform" and the actual populations are the same, while for all others, the "uniform" populations give a greater fraction of the total electron density in less stable e_g orbitals and a smaller fraction in the

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[9] It is possible that under exceptional circumstances, the d^n configuration might become less stable than, say, a $d^{n-1}s$ or $d^{n-1}p$ configuration, which might have a different number of unpaired electrons. However, no certain instance of such behavior is actually known and it is not necessary to bring this possibility up in an introductory treatment of ligand field theory.

[10] See, for example, COTTON AND WILKINSON, p. 582 ff.

Table 1. Actual and "Uniform" Orbital Populations in an Octahedral Ligand Field

Total "*d*" electrons		0	1	2	3	4	5	6	7	8	9	10
"Uniform" populations	e_g	0	$^2/_5$	$^4/_5$	$^6/_5$	$^8/_5$	2	$^{12}/_5$	$^{14}/_5$	$^{16}/_5$	$^{18}/_5$	4
	t_{2g}	0	$^3/_5$	$^6/_5$	$^9/_5$	$^{12}/_5$	3	$^{18}/_5$	$^{21}/_5$	$^{24}/_5$	$^{27}/_5$	6
Actual populations	e_g	0	0	0	0	1	2	2	2	2	3	4
	t_{2g}	0	1	2	3	3	3	4	5	6	6	6
Stability differences		0	$^2/_5$	$^4/_5$	$^6/_5$	$^3/_5$	0	$^2/_5$	$^4/_5$	$^6/_5$	$^3/_5$	0

more stable t_{2g} orbitals. Since there are differences in the occupation of the more and less stable orbitals, there are differences in the energies of the "uniform" and the actual configurations.

For the d^1 case, to go from the uniform to the actual configuration, $^2/_5$ electron is transferred from the e_g to the t_{2g} orbitals. There is thus a stability increase (energy decrease) of $^2/_5\Delta_0$. Again, for the d^7 case, $^4/_5$ electron is transferred from e_g to t_{2g} orbitals, causing an increase of $^4/_5\Delta_0$ in the stability. The stability differences so obtained for all the d^n ions are listed, in units of Δ_0 for each ion, in Table 2.

Table 2. Ligand Field Stabilization Energies in Octahedral and Tetrahedral Ligand Fields

No. of electrons	LFSE[a] Oct	LFSE[a] Tetra
0	0	0
1	$^2/_5\ \Delta_0$	$^3/_5\ \Delta_t$
2	$^4/_5\ \Delta_0$	$^6/_5\ \Delta_t$
3	$^6/_5\ \Delta_0$	$^4/_5\ \Delta_t$
4	$^3/_5\ \Delta_0$	$^2/_5\ \Delta_t$
5	0	0
6	$^2/_5\ \Delta_0$	$^3/_5\ \Delta_t$
7	$^4/_5\ \Delta_0$	$^6/_5\ \Delta_t$
8	$^6/_5\ \Delta_0$	$^4/_5\ \Delta_t$
9	$^3/_5\ \Delta_0$	$^2/_5\ \Delta_t$
10	0	0

[a] Δ_t is generally $\leqslant {}^1/_2\ \Delta_0$ for a given ion with common ligands.

These results may now be compared with some experimental data. Figure 12 shows the heats of hydration, as given by the reaction:

$$M^{2+}(g) + \infty H_2O\ (l) = [M(H_2O)_6]^{2+}\ (aq)$$

for all the known dipositive ions of the first transition series. It is seen that these heats do not vary uniformly, though the irregularities are only small fractions ($\leq$30 kcal/mole) of the total energies (600–700 kcal/mole). This is because the number of "non-uniformly" distributed electrons is only a small fraction of the total number. Further, if a smooth curve is drawn through the points for the three ions (Ca^{2+}, d^0; Mn^{2+}, d^5; and Zn^{2+}, d^{10}) which do, in fact, have uniform populations, all other points lie above it. Qualitatively, this is just what we should expect. In all cases, the electrons are equally distributed among the *d* orbitals of the free ions, M^{2+}, and in the three cases, d^0, d^5, d^{10} they continue to be so distributed in the $[M(H_2O)_6]^{2+}$ ions; in the remaining cases, they move completely or more completely to the more stable orbitals, thus releasing additional energy. These additional energies are called *ligand field stabilization energies*, LFSE's. If the values of Δ_0 are known (as they are from spectral data, see later) the LFSE's can be calculated, and when they are subtracted from the actual heats of hydration, points are obtained which lie very close to a smooth curve through the experimental points for the d^0, d^5, and d^{10} ions, that is, to the values which would be interpolated for other ions, if those ions had "uniformly" filled *d*-like orbitals. This is only a first approximation, however, since there are other effects, such as the non-uniform variation of ionic radii, to be discussed shortly, which must be considered; these effects are not believed to be large (*8*).

Similar results are obtained for lattice energies and for the energies of other processes where complexes are formed; see George and McClure for general background and reference (*9*) for some more recent results. By reasoning analogous to that embodied in Table 1, the LFSE's for tetrahedral complexes can be deduced. These are also given in Table 2.

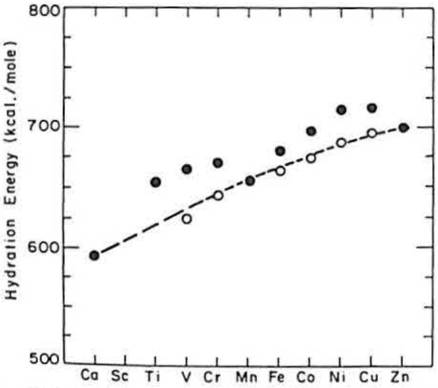

Figure 12. Hydration energies of divalent ions of the first transition series. Solid circles are experimental values; open circles are obtained by subtracting the calculated LFSE's from the experimental values.

Using the octahedral and tetrahedral results together, another interesting phenomenon may be explained. If is known that as we go from Mn^{2+} to Zn^{2+}, there are great irregularities in the tendency to form tetrahedral complexes. Generally speaking there is an increase, but Co^{2+} is abnormally prone to do so, whereas Ni^{2+} especially and also Cu^{2+} seem definitely to prefer octahedral coordination. From the figures in Table 2 these facts may be qualitatively explained. For Co^{2+} (d^7) we have the largest tetrahedral LFSE together with an average octahedral LFSE, while with Ni^{2+} we have the largest octahedral LFSE together with an average tetrahedral LFSE. For Cu^{2+} the octahedral LFSE also exceeds the tetrahedral by a relatively large amount, but here the existence of considerable distortions in both the octahedral and tetrahedral complexes requires caution in pressing the LFSE argument. It has recently been found (*9*) that the LFSE's can almost quantitatively account for the irregular energies of the processes

$$[MCl_4]^{2+}\ (g) + 6\ H_2O\ (g) = [M(H_2O)_6]^{2+}\ (g) + 4\ Cl^-\ (g)$$

Some Stereochemical Consequences

There are two striking examples of the effect of *d* orbital splittings on stereochemistry which can reasonably be covered in a discussion of LFT at the introductory level.

The first is the irregular variation in the radii of the divalent ions of the first transition series, which again provide the best grist for our mill, since they have been most thoroughly studied. The radii of these ions would be expected to show an overall decrease since the nuclear charge is increased through the series, while the electrons added to the *d* shell screen one another imperfectly. This overall decrease in radii is observed, but, as shown in Figure 13, it is not a smooth one.

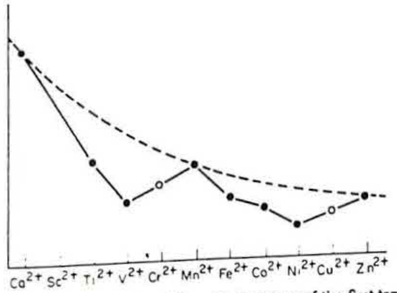

Figure 13. Relative ionic radii of the divalent ions of the first transition series. The Cr^{2+} and Cu^{2+} points are somewhat uncertain because of the distorted octahedra in which these ions are found.

The occurrence of the two "festoons" is a consequence of the *d* electron configurations. We recall that the t_{2g} electrons are nonbonding electrons (at least to a first approximation) while the e_g electrons are antibonding: that is, their presence tends to *weaken and thus lengthen* the metal ligand bonds. We therefore expect the metal ligand bond lengths to be little affected by the presence of t_{2g} electrons, but to be fairly sensitive to the presence of e_g electrons, lengthening in proportion to the number of such electrons.

In Figure 13, a smooth curve has been drawn through the points for the d^0, d^5, and d^{10} ions. This curve may be considered to indicate the expected radii for ions having electrons equally distributed among all the *d* orbitals, as do the d^0 (all orbitals empty), d^5 (all orbitals half-filled), and d^{10} (all orbitals completely filled) ions. Thus, for Ti^{2+}, the d^2 ion, this would be the radius if it had $^4/_5$ electron in the e_g orbitals; actually the d^2 ion has no electron at all in the e_g orbitals, the bonds to the ligands are therefore shorter and the radius of the ion is taken to be less than the value indicated by the curve. For the d^3 ion, V^{2+}, the actual number of e_g electrons is $^6/_5$ less than the number corresponding to the curve and the actual radius is again, and even more markedly, less than that indicated by the curve. In the next two ions, which have $t_{2g}^3e_g$ and $t_{2g}^3e_g^2$ configurations, the number of e_g electrons increases and reaches the value corresponding to the curve. In the second half of the group, the same sequence of configurations recurs, superposed on the $t_{2g}^3e_g^2$ configuration reached at Mn^{2+}, and the second festoon thereby results.

The second striking structural result of *d* orbital splitting is found (*10*) among the class of compounds called *spinels*. These are oxides whose most general formula is $ABCO_4$, where A, B and C are cations, the sum of whose charges is +8. In many cases, such as the mineral spinel, $MgAl_2O_4$, which gives its name to the class, B = C, and in still others, all the cations have the same atomic number, e.g., Fe_3O_4, Mn_3O_4 and Co_3O_4. The spinel structure can be described as a cubic close-packed array of oxide ions with one-third of the cations occupying tetrahedral interstices and the remaining two thirds occupying octahedral interstices.[11] The "normal" spinel structure, when the charges on the ions are +2, +3 and +3, has the +2 ions in the tetrahedral holes and the +3 ions in the octahedral ones, and it can be shown that for ions which are spherical this arrangement should be, to some slight extent at least, the favored one.

There are cases, however, in which the divalent ions occupy octahedral holes along with half the trivalent ions, while the other half of the trivalent ions go into the tetrahedral holes normally occupied by the divalent ions. In every case where such an inversion has been found, it can be explained in terms of LFSE's. For instance, Fe_3O_4 is inverted, while Mn_3O_4 and Co_3O_4 are normal. To invert Mn_3O_4, Mn^{3+} ions which are in octahedral holes, would have to be transferred to tetrahedral ones, with a loss in LFSE (see Table 2), while Mn^{2+} ions, which have no LFSE in either environment, would have to be shifted from tetrahedral to octahedral holes. Thus, the overall result would be a loss of LFSE, and inversion does not occur. For Co_3O_4, inversion would be extremely disfavored, due to the large LFSE's of both the low-spin Co^{3+} ions in the octahedral holes and the Co^{2+} ions in the tetrahedral ones, and, again, it does not occur. For Fe_3O_4, however, the inversion is favorable insofar as LFSE goes, since transfer of high-spin d^5 Fe^{3+} from octahedral to tetrahedral holes carries no penalty, while transfer of high-spin d^6 Fe^{2+} from tetrahedral to octahedral holes produces a net gain in LFSE.

Still another example is provided by $NiAl_2O_4$, which is inverse. Here transfer of Al^{3+} does not change the net LFSE, but transfer of Ni^{2+} from the tetrahedral to the octahedral holes is strongly favored.

It should be emphasized that these inversions could not have been predicted *ab initio*, since this would require more detailed understanding of *all* the energy terms than was, or still is, generally available; but given the empirical fact that the normal and inverse structures are similar in stability in the absence of LFSE effects, we have very good indications of where and where not to expect inverse structures to occur.

Visible Spectra of Transition Metal Compounds

Surely one of the most striking characteristics of the transition elements is the fact that nearly all of their compounds are colored and the colors are extremely varied. Even at the introductory level—perhaps especially at this level—an attempt to explain this, at least in correct qualitative fashion, would be worthwhile and interesting to the students. Such an explanation provides a good opportunity to correlate what may be isolated ideas in the student's minds, for example, the relationship between the color of a substance and the positions of its absorption bands, and the relationships of these in turn to the transitions between electronic energy levels.

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[11] A help in visualizing these structures may be the use of models such as those described by LAMBERT, J. L., J. CHEM. EDUC., 41, 41 (1964).

There are however limitations on what can be done, since a complete understanding of the electronic states of the multi-electron ions, d^2–d^9, requires far more discussion than would seem feasible in the usual introductory course devoted to a comprehensive survey of chemistry. In the following paragraphs, the sort of coverage which seems to this writer to be feasible is outlined.

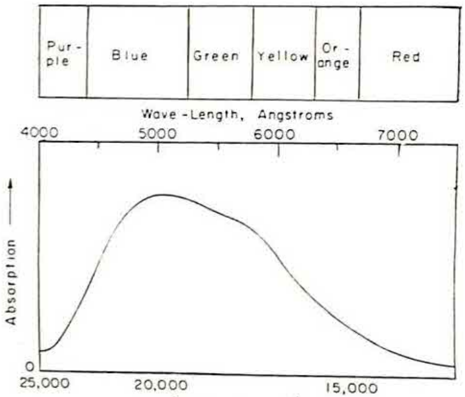

Figure 14. The visible absorption spectrum of $[Ti(H_2O)_6]^{3+}$.

The spectra of d^1 ions can be covered without difficulty. For a d^1 ion in a regular octahedral field, the $[Ti(H_2O)_6]^{3+}$ ion is a good example; its spectrum, shown in Figure 14, consists of only one band centered at about 20,000 cm^{-1} (5000 Å). This can be identified as arising from excitation of the electron from the t_{2g} to the e_g orbitals, and its energy corresponds to Δ_0. Thus, from the spectrum we are able to determine that Δ_0 is 20,000 cm^{-1} or 57.2 kcal/mole.[12] The pale, red-purple color of the $[Ti(H_2O)_6]^{3+}$ ion is due to the fact that this absorption band is so placed as to allow most of the red light and some of the blue light to pass through unabsorbed and the combination of these two transmission bands produces the red-purple color we see. Figure 14 also shows where the principal colors occur in the visible spectrum, which extends, approximately, from 4000 to 7500 Å.

Another good example, which can be demonstrated easily, of the relationship between color and spectrum is provided by the Ni^{2+} ion. In a pale green solution of nickel sulfate in water, the color is caused by $[Ni(H_2O)_6]^{2+}$ ions. On adding ethylenediamine, the color turns deep blue, because of the formation of the $[Ni\ en_3]^{2+}$ ion. The spectra of these two solutions are shown in Figure 15. Again a "color map" of the visible region is given. It is easily seen that $[Ni(H_2O)_6]^{2+}$ has a minimum in its absorption where green light occurs, but absorbs nearly all the rest of the light seen by the eye; hence it appears green. $[Ni\ en_3]^{2+}$, on the other hand absorbs green light strongly and also yellow, orange, some blue and some red light; it transmits only blue-purple light and a little red light.

The spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni\ en_3]^{2+}$ illustrate the basis of the *spectrochemical series* of ligands. Since the energies of the absorption bands of Ni^{2+} in its complexes are proportional to the splitting of the d orbitals by the ligands, it is evident that the electrons on the six nitrogen atoms provided by the three ethylenediamine molecules interact more strongly with the d orbitals and hence cause a greater energy difference between the e_g and t_{2g} orbitals than do the electrons on the six oxygen atoms of the water molecules. It has been found that for *every* transition metal ion of common occurrence, replacement of $2n$ H_2O's by n ethylenediamines causes the absorption bands to shift to higher energies (shorter wavelengths). Moreover, a rather long list of ligands can be arranged in the order of the energies of the absorption bands for any given ion and it is then found that this same order, with, at most, only slight and occasional deviations, is obtained for all the common transition metal ions. This ordering of ligands is called the spectrochemical series, and is as follows, for some of the more familiar ligands:

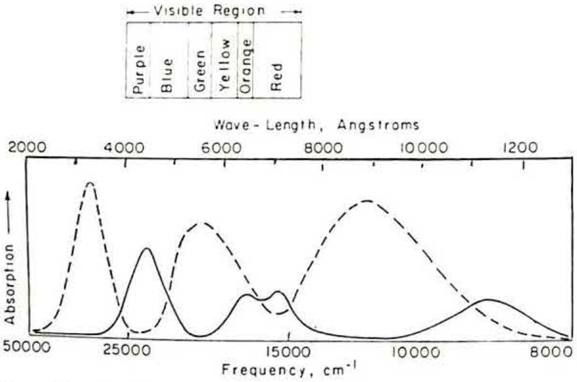

Figure 15. The electronic spectra of $[Ni(H_2O)_6]^{2+}$ (———) and $[Ni\ en_3]^{2+}$ (- - - - - -). A "color map" of the visible region is also given.

$$I^- < Br^- < Cl^- < H_2O \sim \text{many other oxygen ligands} < NH_3 \sim \text{many nitrogen ligands} < \text{en} < CN^-$$

The existence of such a consistent order of d orbital splittings would not necessarily have been predicted theoretically, but it is plausible. It is of considerable value in understanding, correlating and interpreting many observable changes which occur when ligands are added to solutions of transition metal ions.

For metal ions with more than one d electron, detailed explanation of the observed absorption bands seems beyond the scope of an introductory course. For such ions, there are more than two ways (configurations) of arranging the d electrons in the orbitals and each of these configurations gives rise to more than one energy state, because the electrons interact with one another in various ways, as well as with the nucleus and with the ligands. Perhaps the nickel(II) ion can be used to illustrate, though not explain, the nature of this rather complex situation.

There are three possible configurations for eight d electrons in an octahedral ligand field: $t_{2g}^6e_g^2$ (most stable), $t_{2g}^5e_g^3$ (next most stable), and $t_{2g}^4e_g^4$ (least stable). When all of the possibilities for interaction between the electrons are considered it is found that the $t_{2g}^6e_g^2$ configuration gives rise to one state with two unpaired electrons, which is most stable, but also to two other states in which the two e_g electrons have their spins opposed. The $t_{2g}^5e_g^3$ configuration gives rise to four states, two of which have two unpaired electron spins. The highest energy configuration, $t_{2g}^4e_g^4$, gives rise to four states, only one of which has two unpaired electron spins. Since there is a general rule in molecular quantum mechanics that significant absorption of light can occur only when the resulting transition of electrons takes place without change in the number of unpaired electron spins, the appearance of just three absorption bands in the spectra of octahedrally coordinated Ni^{2+} ions is easily understood. The transitions are from the state of the $t_{2g}^6e_g^2$ configuration with two unpaired electrons to the two states of the $t_{2g}^5e_g^3$ configuration with two unpaired electrons and to the one state of the $t_{2g}^4e_g^4$ configuration which has two unpaired electrons.

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[12] For converting spectral energies in their usual units of cm^{-1} to chemical energies in their usual units of kcal/mole, the conversion factor is: 350 cm^{-1} = 1 kcal/mole. Recall that energy (per mole) = $Nh\nu$ = Nh[illegible]

Epilogue

With due acknowledgment to G. B. Shaw for the inspiration, it might be said that theories of chemical bonding—neglecting not a few which are entirely valueless—fall into one of two categories: those which are too good to be true and those which are too true to be good. "True" in this context is intended to mean "having physical validity" and "good" to mean "providing useful results, especially quantitative ones, with a relatively small amount of computational effort." The proper, rigorous wave equation for any molecular situation represents a theory of that situation which is too true to be good. Most theories which are too good to be true are those in which the real problem per se is not treated, but rather an artificial analogue to the real problem, contrived so as to make the mathematics tractable, is set up and solved.

The electrostatic crystal field theory, using the point charge approximation, is such a theory—at its best, or,

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A Selected Annotated Bibliography

Essentially Nonmathematical Comprehensive Accounts

COTTON, F. A., AND WILKINSON, G., "Advanced Inorganic Chemistry, A Comprehensive Text," Interscience, New York, 1962. Chapter 26 gives a general account of LFT suitable for undergraduate students, though probably not for the average freshman without supplementary material. Chapter 29 on the elements of the first transition series discusses the electronic structures of many compounds and complexes in terms of LFT.

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perhaps, at its worst. It is a gift horse which, when looked straight in the mouth, is found to have false teeth. There is no physical validity to it even though it is mathematically convenient and "works" up to a point.

Thus, the conceptually simple picture which has traditionally been employed in introducing the idea of *d* orbital splitting can no longer be used unless one is willing to perpetrate a deliberate and conscious deception. Naturally, it has long been recognized that the crystal field theory could not be taken literally; that is, that a purely electrostatic treatment of complexes and crystals which took no account at all of covalent character in the metal-ligand bonds was not entirely correct. But it was generally assumed that the electrostatic approach was partially or qualitatively, perhaps, in some cases, even semiquantitatively valid, and thus perfectly legitimate for use at least as a first approximation, or as a half truth which further study would not contradict, but merely qualify and enlarge upon. I believe that most teachers at some time find it necessary to use the general approach of beginning a topic with a facile half truth and that this is fair practice. I do not believe, however, that it is ever justified to present, consciously, a facile *untruth*, however much it may help in "putting the subject across." I hope that readers who agree with this premise will find this discussion useful in avoiding some of the untruths about ligand field theory.

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Teaching Organic Stereochemistry

Organic chemistry may be divided into two aspects: the static (molecular architecture, physical properties, and nomenclature) and the dynamic (reactivity and mechanism). In both areas, stereochemical concepts are of prime importance. In molecular architecture, corresponding to *structure* (which denotes the number and kind of atoms in the molecule and the manner in which they are linked), there are the stereochemical concepts of *configuration* (denoting the arrangement of the atoms in three-dimensional space) and *conformation* (the spatial arrangements possible by virtue of rotation about single bonds). Physical properties, such as dipole moments, ultraviolet, infrared, and nuclear magnetic resonance spectra, acid and base strength, etc., depend on stereochemistry as well as structure. Nomenclature has not only structural but also configurational aspects—now, embodied no longer in the old projectional D-L but in the new, truly three-dimensional R–S system (*1*, *2*). A knowledge of configuration (relative and absolute) as well as structure is required before we can consider the question of the architecture of a molecule settled—and rightly so, for molecules of identical structure but differing configuration often have vastly different functions in the realm of nature. Differences in reactivity may reflect differences in stereochemistry as much as differences in functionality. Many reactions are known which are "stereoselective" (*2*) meaning that of two possible stereoisomeric products, one is formed in considerable predominance over the other. Such stereoselectivity tends to be particularly marked in biological systems which often produce one stereoisomer to the total exclusion of the other, as for example in the hydration of fumaric acid in the presence of the enzyme fumarase which produces (−)-malic acid uncontaminated by the dextrorotatory isomer. Other reactions are "stereospecific" (*2*) meaning that of two stereoisomeric starting materials one gives a different product from the other (usually the two products are also stereoisomers). An extreme example, again from biochemistry, is one where only one stereoisomer enters into reaction and the other does not. Thus fumarase catalyzes the hydration of fumaric acid to (−)-malic acid but it does not catalyze the hydration of maleic acid, the cis isomer of fumaric acid. One of the earliest discoveries in this area was made by Pasteur (*3*) more than 100 years ago who found that the mold *Penicillium glaucum* ferments the naturally occurring (+)-tartaric acid but leaves the enantiomeric (−)-tartaric acid untouched. Besides these obviously significant biological implications of dynamic stereochemistry, it is also important in establishing and understanding reaction mechanisms. Conformational principles, especially, play an important role in this area.

Teaching Stereochemistry

There are three levels at which, in the author's opinion, stereochemistry can and should be taught: the advanced, the elementary, and the preparatory. A thorough treatment is in order at the advanced undergraduate or early graduate level, following a basic understanding of both organic and physical chemistry. The author has recently written a textbook (*2*) to help with this particular task. There are several ways in which the material can be presented. The conventional way—through a formal lecture course—will probably take two hours per week for a semester or three hours per week for a quarter. An alternate method might be to ask the students to read the textbook in 12–15 weekly doses and to devote one class period per week to answering questions on difficult points and to explaining highlights. This period might be one of three otherwise devoted to a course in reaction mechanisms or organic chemistry. Preferably such a reading-recitation arrangement should be supplemented with problem work.

Of much greater scope than the advanced-level teaching of stereochemistry is the teaching of the subject at the elementary organic (sophomore or junior) level.[1] Here the author has strong feelings as to the proper and improper way of handling the subject. He feels, quite uncompromisingly, that stereochemistry should be integrated with organic chemistry as a whole (starting with a model of methane and ending with DNA) and should not be taught as an appendage after most of organic chemistry has been dealt with in two dimensions. This strong feeling is based on personal learning experience, on the experience with a number of students who were taught the wrong way and never did grasp stereochemistry properly, and with more recent experience with students who not only assimilate stereochemical ideas early in the organic course with great fascination and enthusiasm but also emerge from the course with a real understanding of stereochemical concepts. It was a great disappointment, therefore, to find upon surveying the seven most popular organic

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This article is based upon a paper presented as a part of the Symposium on Three-Dimensional Chemistry before the Division of Chemical Education at the 144th Meeting of the American Chemical Society, Los Angeles, California, April, 1963.

[1] At the University of Notre Dame, after teaching organic chemistry to the chemistry and chemical engineering majors at the sophomore level for many years, it has now been shifted back to the junior level with physical chemistry being taught in the sophomore year. It is believed that this will allow us to use much more sophisticated thinking in terms of chemical energetics and kinetics in the teaching of organic chemistry in general and stereochemistry in particular.

textbooks (as of March 1962, according to the Gimelli Report)[2] that only three of them present the subject matter in a thoroughly satisfactory fashion and as many as two handle it in a manner which I would consider quite unsatisfactory. On the other hand, it is gratifying and probably in part indicative of the good sense of chemistry teachers, that the most popular text (used, as of March 1962 in 37% of the schools surveyed) has one of the best treatments. It is certainly to be hoped that future organic texts will have stereochemical concepts (optical and geometrical isomerism as well as conformational principles) presented early so that these concepts can then be illustrated and used appropriately over the entire area of the subject.[3]

Stereochemistry in the General Chemistry Course

The most controversial part of the thesis here presented is that of recommending the teaching of stereochemistry to freshmen. Since so much that was formerly taught at a later stage has now filtered into the freshman course, some undergraduate teachers seem to have become apprehensive about further efforts in this direction. They are particularly hard to convince when the subject matter deals with organic chemistry which is usually and perhaps necessarily taught in only quite cursory fashion at the freshman level and thus does not appear to afford the required background for something as sophisticated as stereochemistry. Also, some freshman teachers are loath to add new subject matter to the curriculum because it obligates them to omit some other subject matter which they consider worthwhile. On the other side of the ledger, the current trend in freshman chemistry courses is to put greater emphasis on principles and to put less effort in an encyclopedic treatment of inorganic chemistry. This makes for a more flexible course, and in the author's opinion, stereochemical principles are among those that deserve to be included. This is particularly true since, as will be demonstrated later, an extensive knowledge of organic chemistry is *not* required for an appreciation of stereochemical principles. In fact, stereochemistry is already touched on in at least two freshman texts, although in so brief a fashion that one may have doubts as to whether the student is being either informed or stimulated. Of more significance in the teaching of stereochemistry to freshmen is the recent appearance of a small supplementary freshman text (*4*) by W. Herz "for beginning students of general science" in which, according to the announcement of the book, "the concepts of conformational analysis and optical and geometrical isomerism, all of which are important to the understanding of biological phenomena, are discussed."

The introduction of stereochemistry to freshmen should be accomplished in two lectures in order not to consume excessive class time. The freshman lectures are definitely not designed to communicate a great amount of detailed information (this can be done later) but rather to generate interest by outlining the basic concepts and pointing out their importance.

The avowed aim of my own freshman lecture is to put across to the student the idea of stereoselectivity and stereospecificity, i.e., to make him realize why a reaction may be stereoselective or stereospecific. It is not difficult to motivate the student toward this study and get him to recognize its importance after he has been told that most of the major components of living matter are dissymmetric and are generated in that form in biochemical syntheses. (In contrast, the classical and more detailed and systematic approach at the sophomore level puts the major stress on optical rotation. Without wishing to belittle the importance of optical rotation and especially of its recent progeny, optical rotatory dispersion (*5*)—which can, for example, be used to follow the denaturation of proteins and of DNA—it must be said that it is largely a diagnostic tool, and to spend too much time on the relationship between dissymmetry and rotation is apt to produce a "so what?" attitude especially on the part of the intellectually more aggressive students.)

The approach which the author chose for the presentation of stereochemical thinking—and which is neither particularly original nor claimed to be necessarily the best approach—begins with a very brief historical discussion of the nature of polarized light (Malus) including the showing of a schematic diagram of a polarimeter, and of the discovery of optically active substances by Aragot and Biot. A second schematic diagram shows the effect of optically active substances on the plane of polarized light and serves to introduced the terms "angle of rotation," "dextrorotatory" and "levorotatory." The term "specific rotation" may also be introduced here by pointing out that rotation is proportional to the number of molecules encountered and that in order to obtain a quantity characteristic of a particular substance, one must divide by concentration and cell length. However, no great stress need be put on this term, in as much as it is not very important in the development of the major overall ideas. It is next pointed out that some substances, such as quartz and urea, are optically active only in the solid state so that their optical activity is clearly a property of the crystal. However, other substances, such as turpentine, sugar, tartaric acid are active as solids, liquids, gases, or in solution so that there the activity is evidently a property of the molecule. Pasteur's suggestion that optical activity is related to molecular dissymmetry is next introduced, the right and left hand being used as examples of dissymmetric, mirror-image objects. The term "enantiomer" is also introduced here. Van't Hoff's picture of the tetrahedral carbon of type *Cabcd* (Fig. 1, top) as the focus of dissymmetry is now presented with a showing of pictures and models of enantiomeric molecules. The concept of configuration is touched on by saying that in any given instance, there is a real problem of determining which of the two arrangements of *Cabcd* corresponds to the dextrorotatory and which to the levorotatory form. (This problem of configurational assignment may be likened to the structural problem of determining whether C_2H_6O is ethyl alcohol or diethyl ether—if the students know enough organic chemistry at this stage. Unfortunately, it seems beyond the scope of a freshman lecture to try to indicate a solution to the problem of configurational assignment.) Lactic acid is presented at this point as a simple molecule which has two enantiomers both of which occur naturally. To impress upon the student that optically active materials are widely distributed in nature, the rotation of a steroid (e.g., cholesterol), an alkaloid (e.g., quinine), a sugar (e.g., sucrose), a polypeptide or protein (e.g., oxytocin), and a nucleic acid (e.g., DNA) are presented next. (Only the names of the compounds and their specific rotations are shown assuming that the students' background in organic chemistry at this stage is insufficient for them to appreciate the structural formulas.)

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[2] GIMELLI, S. P., Private communication to the author from a committee report submitted March 25, 1962 to the Organic Subcommittee of the Examinations Committee of the Division of Chemical Education, ACS.

[3] The author has examined two major organic texts which appeared in 1963. Unfortunately, stereochemistry is taken up early in only one of them, and even in that one it is not fully integrated in the fabric of the subject matter.

At this point, the student begins to see the importance of enantiomerism in nature. One must now explain to him that the synthesis of dissymmetric substances does not ordinarily lead to optically active materials. The synthesis of *Cabcd* from *Caabc* (inactive) is presented in this context and is illustrated by the formation of α-bromopropionic acid by bromination of propionic acid. The student easily sees that both enantiomers are formed with equal ease and the concept of a racemic modification as an assembly of equal number of dextro- and levorotatory molecules develops logically. It is next explained (and exemplified) that enantiomers are identical in all ordinary physical and chemical properties (except for sign of rotation) as well as in internal energy; again this may be rationalized through an analogy with an individual with perfectly shaped hands. (The relation between any two fingers of the right hand (say the thumb and the ring finger) is the same as the corresponding relation in the left hand—in fact, the terms "right" and "left" are meaningful only in the presence of some (external) orienting coordinate system.) Besides being indeed very similar, enantiomers are also equally reactive toward a symmetrical reagent. Again our analogy may be used: if the individual with perfectly shaped hands is also ambidextrous, he will be able to handle a symmetrical tool, such as a hammer, equally well with either hand.

By now the student is curious how optically active molecules can originate at all. His attention is therefore drawn to the fact that toward a dissymmetric "reagent," such as a glove, the two hands are not equal at all. (A better analogy may be that of a right-and left-handed screw—when turned into a symmetrical wooden board, the two behave essentially the same, but toward an unsymmetrical right-handed nut, they behave very differently.) In fact, one may write such mock reactions as

right hand + right glove → gloved hand (fast reaction)

right hand + left glove → no reaction

This serves as an analogy for the high stereospecificity of certain chemical reactions.

The lecture now enters its most difficult phase where the students find it hardest to keep up with the ideas. It is therefore well to strengthen their interest with a few more examples of enantiomers which behave differently in a dissymmetric environment: that of asparagine where only one of the two enantiomers tastes sweet to man (who, because of all the proteins in his enzyme systems, is highly dissymmetric chemically speaking); that of glutamic acid where one enantiomer but not the other is a well-known flavor-enhancing agent; and that of the antibiotic chloromycetin which, like many drugs, is effective only in one of its enantiomeric forms. The earlier-mentioned case of the fermentation of the natural (+) but not the unnatural (−)-tartaric acid by the enzyme systems of *Penicillium glaucum* may also be presented at this stage.

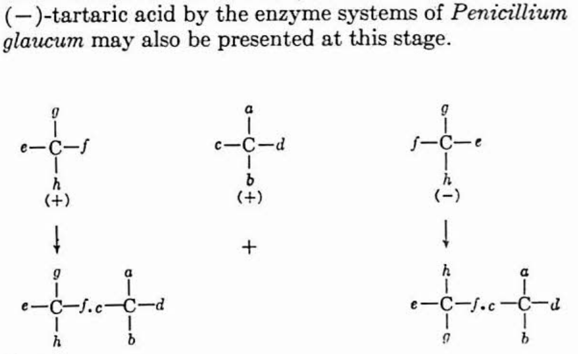
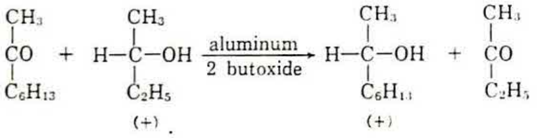


Figure 1.

The molecular basis of the right-hand-right-glove and right-hand-left-glove analogy may now be shown as indicated in Figure 1. The two enantiomers (+) and (−)-*Cefgh* react with a single enantiomer of *Cabcd*. The reactive spot of the molecules where interaction occurs is assumed to be at *c* and *f*. It is clear that (−)-*Cefgh* must be turned upside down for the reaction to be written and that the two resulting molecules *Cabcd*, *Cefgh*, while stereoisomers, are no longer enantiomeric (mirror images). These molecules, it is explained are called diastereoisomers (nonenantiomeric stereoisomers) and differ in their physical and chemical properties and internal energy as much as other pairs of (structural) isomers might because the internal relationships in diastereoisomers, unlike those in enantiomers, are no longer the same. (As written in Figure 1, the product on the left has *a* close to *g* and remote from *h*, whereas in the molecule on the right, *a* is close to *h* and remote from *g*. If *a* and *h* can engage in intramolecular hydrogen bonding, for example, the second combination may well be the more stable one.) Now (+)- and (−)-tartaric acid and *meso*tartaric acid are presented as a set of stereoisomers containing both enantiomers and diastereoisomers and the difference in properties of the diastereoisomers is shown. (Some instructors may prefer to show only one enantiomer of active tartaric acid along with the meso form in order not to complicate the picture unnecessarily.) To drive home the difference in reactivity and properties of diastereoisomers, one may introduce yet another mechanical analogy: the difference of a right-hand-right-baseball glove and right-hand-left-baseball glove combination in compactness, feel, and possible reaction toward a flying baseball.

The student may now begin to grasp the difference in reactivity between stereoisomers when both starting materials are dissymmetric. However, he does not yet have the basis to understand the asymmetric synthesis involved when active compounds arise from inactive precursors in biological systems. In order to make him understand this requires a consideration of transition state energetics and therefore some prior knowledge of energy profiles. Granted that knowledge, the underlying principle can be illustrated by the example shown in Figure 2. The reduction of methyl isohexyl ketone (inactive) with (+)-2-butanol through a hydride transfer gives, in addition to inactive 2-butanone, (+)-2-methylisohexylcarbinol in predominance over the (−)-isomer. Clearly the pair of starting materials as well as the pair of products are enantiomeric, not diastereoisomeric and the preference thus seems at first sight surprising. The reason why there can yet be asymmetric synthesis is that in the transition state, both the asymmetry of the 2-butanol (A) and that of the incipient methylhexylcarbinol (B) are present and therefore there are two possible transition states, (+)-A. . .(+)-B and (+)-A. . .(−)-B, which are diastereoisomeric and therefore unequal in energy; the first happens to be preferred. The energetic situation is as diagramed in Figure 3.



$$\underset{C_6H_{13}}{\overset{CH_3}{CO}} + \underset{\underset{(+)}{C_2H_5}}{\overset{CH_3}{H-C-OH}} \xrightarrow[\text{2 butoxide}]{\text{aluminum}} \underset{\underset{(+)}{C_6H_{13}}}{\overset{CH_3}{H-C-OH}} + \underset{C_2H_5}{\overset{CH_3}{CO}}$$

Figure 2.

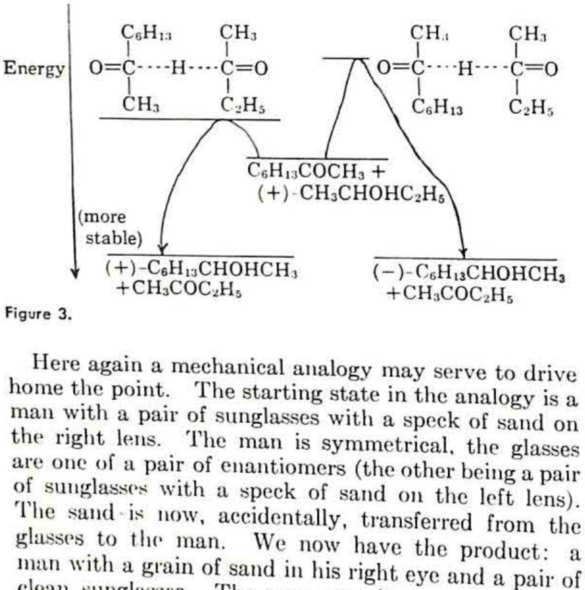

Energy
$O{=}\underset{CH_3}{\overset{C_6H_{13}}{C}}\cdots H\cdots \underset{C_2H_5}{\overset{CH_3}{C}}{=}O$
$O{=}\underset{C_6H_{13}}{\overset{CH_3}{C}}\cdots H\cdots \underset{C_2H_5}{\overset{CH_3}{C}}{=}O$
$C_6H_{13}COCH_3$ +
(+)-$CH_3CHOHC_2H_5$
(more stable)
(+)-$C_6H_{13}CHOHCH_3$ +$CH_3COC_2H_5$
(−)-$C_6H_{13}CHOHCH_3$ +$CH_3COC_2H_5$

Figure 3.

Here again a mechanical analogy may serve to drive home the point. The starting state in the analogy is a man with a pair of sunglasses with a speck of sand on the right lens. The man is symmetrical, the glasses are one of a pair of enantiomers (the other being a pair of sunglasses with a speck of sand on the left lens). The sand is now, accidentally, transferred from the glasses to the man. We now have the product: a man with a grain of sand in his right eye and a pair of clean sunglasses. The man now is one of a pair of enantiomers and the glasses are symmetrical. Nevertheless, the reaction is completely stereoselective: the grain of sand is only transferred to the right eye, not to the left eye. This is because the two possible transition states, one in which the sand is transferred from the right lens to the right eye, and the other in which it is transferred from the right lens to the left eye are diastereoisomeric; and in fact, the latter will be much higher in energy than the former, so to speak.[4]

This is probably as far (or perhaps a little farther) than one can go in a freshman lecture. One may conclude the lecture by saying that while the principles of asymmetric synthesis, stereospecificity and stereoselectivity are now clear, the actual detailed mechanism remains to be elucidated.[5] (In fact, much research is going on at the present time on understanding the stereospecificity and stereoselectivity of enzymes. Other problems which have but been referred to are the elucidation of configuration, the actual practical methods of obtaining optically active compounds and the origin of optical rotation in an asymmetric molecule. Some important topics, such as conformational analysis, have not been mentioned at all.

One of the ways of illustrating the scope of the lecture is by means of the quiz given following the presentation. The results showed quite a significant level of absorption of the material presented. They also pointed out certain shortcomings which will be avoided on future occasions. One, already mentioned, is that the lecture was too compressed. It should be extended over two hours. Another was that the material was presented too early in the course, following a treatment of the structure of organic compounds near the end of the fall semester. Better results could undoubtedly have been achieved had the lecture been given in the second semester—either near the beginning, following an elementary treatment of the thermodynamics of chemical reaction and chemical kinetics, or near the end, as part of a series of specialized topics in organic chemistry. Despite this, the results were sufficiently promising to make us decide to repeat the experiment in the following academic year. The author hopes other freshman instructors will be encouraged to perform it also.

Questions on Stereochemistry for Freshman Chemistry Students

1. What is meant by the statement, "An optically active substance is dextrorotatory?" Would such behavior depend on the state of aggregation? Explain.

2. What are enantiomers? What is meant by the statement, "Enantiomers differ in configuration?" What is the source of enantiomerism at the molecular level?

3. What is meant by "specific rotation?" If a substance shows a rotation of 5.00° when viewed in a 2-dm cell in a solution of concentration 0.1 g/ml, what is the specific rotation of the substance? (The dm or decimeter and the concentration in g/ml are the proper units for the expression of specific rotation.)

4. Suppose you have two beakers containing racemic tartaric acid in aqueous solution. In beaker 1, half the tartaric acid is destroyed by chemical oxidation, e.g., by permanganate. In beaker 2, half the tartaric acid is destroyed by fermentation by the mold *Penicillium glaucum*. (*a*) What difference exists between the tartaric acid left over in beaker 1 and in beaker 2? (*b*) Explain, as best you can, the reason for this difference.

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[4] The process described in this analogy is, of course, much more highly stereoselective than the chemical reduction of 2-butanone shown in Figures 2 and 3. Its stereoselectivity corresponds more nearly to that of the earlier-mentioned biochemical processes in which, also, the differences in energy between diastereoisomeric transition states are much larger than those shown in Figure 3.

[5] The teacher will be aware, of course, that the picture which has been presented has been in essence a thermodynamic one.

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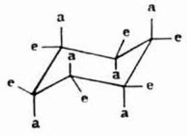
Conformational Analysis in the Elementary Organic Course

As the available information in the field of organic chemistry continues to increase, the teacher of the first-year organic course is faced with an increasingly difficult problem as to which of the many varied and interesting topics available are to be omitted entirely, and which are to be treated only very briefly in the course. Since our understanding of the three-dimensional structure of organic molecules has become much more detailed than it was a decade ago, and since the outcome of so many reactions is dependent on the exact structure of the system, the subject of conformational analysis can scarcely be neglected in any modern introductory course. The subject is now treated briefly in most textbooks, and a rudimentary coverage can be presented in two or three lecture hours.

The prehistoric era of conformational analysis may be considered to have started with the postulation of the tetrahedral carbon by van't Hoff and LeBel in 1874 (*1*), since prior to that time the possibility of the consideration of conformations did not exist. Important early milestones were the postulate by Sachse (1890) of boat and chair forms for cyclohexane (*2*), and experimental evidence for this situation by Hückel (1925) in the preparation of cis and trans isomers of a decalin-like ring system (*3*). The real foundation of conformational analysis was, however, laid down about 1935 when a number of physical chemists, in an effort to explain the discrepancy between the entropy of ethane as found from heat capacity measurements and as calculated from spectral data, slowly came to the conclusion that there must be a hindrance to the rotation about the carbon-carbon bond in ethane (*4*).

These thermochemical measurements showed that there must exist a torsional barrier to free rotation in ethane which was threefold, sinusoidal in shape, and which had a height of about 2.8 kcal/mole (Fig. 1). A similar barrier was found to exist in *n*-butane, but here the minima did not all have the same energy. Superimposed on the torsional barrier to rotation about the central bond was an additional van der Waals' repulsion between the two methyls, such that the anti-conformation gave an energy minimum about 0.8 kcal below that of the gauche minima (Fig. 2).

The most successful applications of conformational analysis to date have been with cyclohexane rings. The basic ideas were introduced by Beckett, Pitzer, and Spitzer in 1947 (*5*) but the real usefulness of these ideas was first illustrated in the important paper by Barton (1950) (*6*). The reason for the particular success in this case is the fact that there exist only two kinds of bonds on the cyclohexane ring, axial and equatorial (I), and a simple substituent can be attached in only two conformationally different ways, which correspond to the anti and gauche minima in butane. Rings other than six-membered have conformations which do not correspond to these energy minima, and the result is that there are usually many non-equivalent ways a substituent may be bound to the ring, and the conformational problem is much more involved. Acyclic compounds are, in general, also complicated conformational mixtures.



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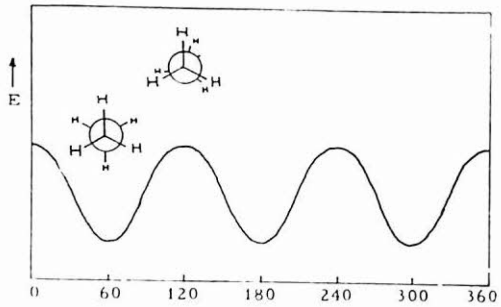

Figure 1. Rotational barriers in ethane.

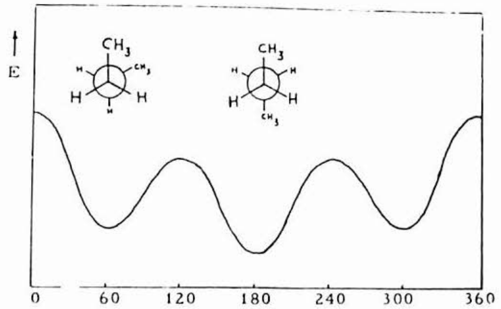

Figure 2. Rotational barriers in butane.

If we take methylcyclohexane as a simple example, we see that there are two conformations, one in which the methyl group is equatorial (I*e*) and one in which it is

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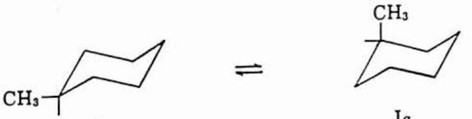
This article is based upon a paper presented as a part of the Symposium on Three-Dimensional Chemistry before the Division of Chemical Education at the 144th Meeting of the American Chemical Society, Los Angeles, California, April, 1963.

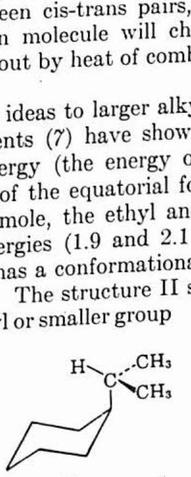
axial (I*a*), and these are in equilibrium. These two conformations differ energetically only because



I*e* I*a*

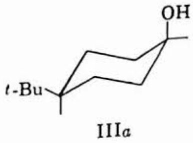
the interactions between the methyl and the ring are different. In I*e*, the methyl group is arranged with respect to the ring carbons 3 and 5 in a manner analogous to the anti arrangement of *n*-butane, while in I*a* the methyl has a gauche arrangement with respect to the same atoms. The energy of the latter form is therefore expected to be the greater than that of the former by about two times 0.8 kcal/mole. In the dimethylcyclohexanes, by summing interactions of this type one can quite accurately predict the energetic relationships between cis-trans pairs, and which conformations a given molecule will choose. Such predictions are borne out by heat of combustion and other experimental data.

Extending these ideas to larger alkyl groups, experimental measurements (*7*) have shown that while the conformational energy (the energy of the axial form minus the energy of the equatorial form) of a methyl group is 1.8 kcal/mole, the ethyl and isopropyl have slightly higher energies (1.9 and 2.1 kcal/mole), and the *t*-butyl group has a conformational energy of more than 5 kcal/mole. The structure II shows why this is true. An isopropyl or smaller group

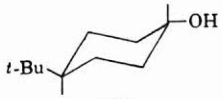


II

can turn in such a way that a hydrogen points back toward the ring, and essentially one has the same kind of gauche interactions for any of these groups. (The exact energy is really a free energy, and it is slightly different for different alkyls because of entropy effects.) With an axial *t*-butyl group in the chair form, however, one of the methyls must point in toward the ring, leading to a very sizeable repulsion. This puts the *t*-butyl group in quite a separate class from the other alkyl groups, a fact not generally appreciated until rather recently (*7*). Since the conformational energy of a *t*-butyl group is so high, under ordinary circumstances it will be found in the equatorial position. This means that molecules like the cis and trans isomers of 4-*t*-butylcyclohexanol have respectively axial and equatorial hydroxyl groups (III*a* and III*e*).

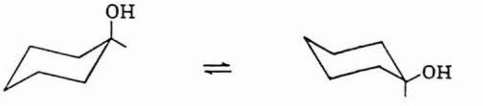


III*a*



III*e*

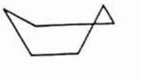
Now, many of the properties of a hydroxyl will vary depending on its axial or equatorial nature. Examples of such properties are the rate of its oxidation to the ketone, or the location of its C—O stretching frequency in the infrared spectrum. If one wishes to study the conformational equilibrium in cyclohexanol itself (IV), since the equilibrium occurs so rapidly at room temperature it is not possible



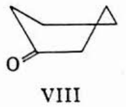
IV*a* IV*e*

to examine the conformations individually. One might expect, however, that by measuring the rate of oxidation of the substance, and by comparing it with the corresponding rates of the axial and equatorial compounds (III*a* and III*e*), the equilibrium constant could be evaluated. The rate is in fact, found to be in between those of the *t*-butylcyclohexanols, and nearer to that of III*e*, indicating that in IV the hydroxyl is found primarily in the equatorial position. Similarly, the ratio of the intensities of the C—O stretching frequencies might be expected to yield an approximate value for the equilibrium constant. A great deal of information has been obtained along these lines regarding chair forms of cyclohexane rings.

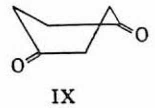
Ever since the prediction by Sachse of the possible existence of a boat form of cyclohexane (V), the question of the existence of such a structure has intrigued organic chemists. The boat form of cyclohexane (somewhat misnamed since the actual form is flexible and the boat conformation is a particular arrangement of the flexible form) can be seen to have two eclipsed units; and therefore, it might be guessed that its energy would be some 5.6 kcal above that of the chair. (Other arrangements of the flexible form are predicted to



V

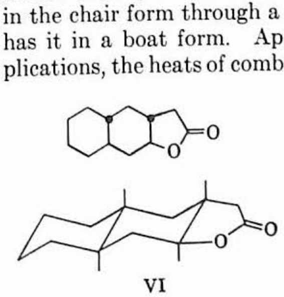


VIII

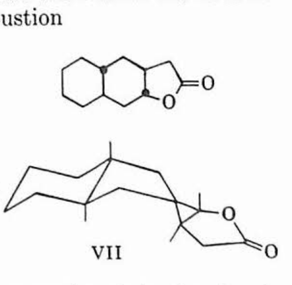


IX

have similar energies.) In a conceptually simple but experimentally quite difficult study, Johnson and his co-workers prepared and established the stereochemistry of the two molecules VI and VII (*8*). The former has the center ring in a chair form, while the latter, since it is not possible to join the adjacent axial positions in the chair form through a five- or six-membered ring, has it in a boat form. Apart from some minor complications, the heats of combustion



VI



VII

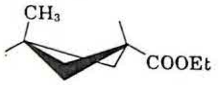
of these compounds gave an experimental value for the conformational energy difference between the boat and chair. These and other similar measurements are all in rather good agreement with the predicted value.

Such a high energy for the boat form of cyclohexane means that it exists in equilibrium with the chair form to the extent of a small fraction of 1% at room temperature. Very rarely are there sufficient constraints in a molecule to make the boat form a significant conformation in a cyclohexane system. In a cyclohexanone system, on the other hand, the situation is somewhat different. As can be seen from structure VIII the cyclohexanone boat as written has only one eclipsed ethane, and therefore a crudely estimated energy of 2.8 kcal/mole. This means that cyclohexanones should be inclined to take up boat conformations much more readily than cyclohexanes, and certainly this has been found to be true experimentally *(9)*.

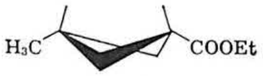
In cyclohexane-1,4-dione (IX), the effect is even more pronounced. Here we calculate that the chair form and the boat form, to a first approximation, should have about the same energy. The experimental evidence indicates that in fact the molecule exists in the boat form *(10)*. The conclusion to be drawn is that while cyclohexane itself is definitely in the chair form, there are various alterations that might occur on a six-membered ring which would tend to stabilize the boat form. In many cases the latter is actually the more stable.

Use of Current Research in Teaching

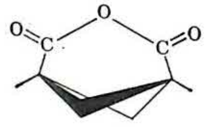
Sometimes in the presentation of this subject it is useful to add a short discussion about some recent conformational problem, since the student can be then made aware at an early stage of his development of the fact that the science is alive and growing, and it will help to relieve the impression sometimes gained by young students that almost everything interesting happened during or before prohibition. Such an example is afforded at the present time by the isomeric 3-methyl-cyclobutane carboxylic acid esters *(11)*.



X *trans*



X *cis*



XI

It is known from spectroscopic and thermodynamic studies that cyclobutane itself has a slightly puckered ring *(12)*. This means that 1,3-disubstituted cyclobutanes such as these will have structures as indicated by X. While intuition might off-hand suggest that the trans isomer should be more stable, the figure shows that the cis isomer can in fact simultaneously get both substituents into more comfortable (equatorial-like) locations. This prediction was made and the esters mentioned were equilibrated in the presence of alkoxide ion. Analysis of the resulting equilibrium mixture by gas phase chromatography showed that the cis isomer, in fact, predominated over the trans at equilibrium. The cis and trans nature of the compounds was proved by virtue of the fact that the cis isomer was prepared via the corresponding diacid which formed a cyclic anhydride (XI), while the trans isomer was prepared from the epimeric diacid which did not form a cyclic anhydride.

The author is of the opinion that a brief exposition of some of the fundamentals of conformational analysis, as outlined above, followed by a few interesting examples of this aspect of modern stereochemistry can greatly increase the students's interest and understanding in organic chemistry. Since there are so many other interesting and important aspects of this subject which must be compressed into this same course, not all instructors will choose to devote the time necessary to cover as much material as is illustrated here. This outline is intended to be a suggestion as to what might be covered, the author himself is, in fact, inclined to be more brief in his own presentation in the elementary course.

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A FRAGMENT OF STEREOCHEMISTRY

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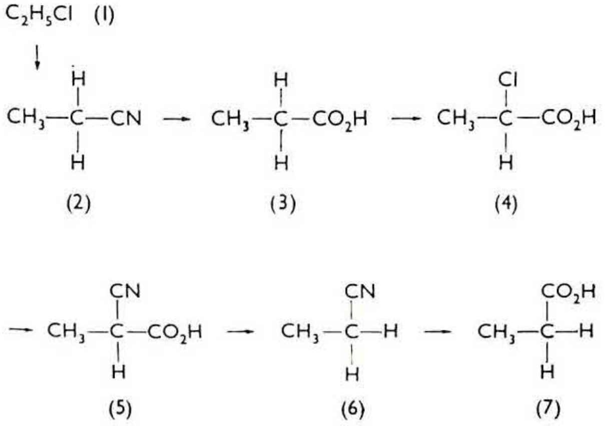
This article provides only a part of the nomenclature of stereochemistry and completely ignores the historical development of the subject. Instead, it indicates the type of information on which our ideas concerning stereochemistry are based

THE TETRAHEDRAL DISTRIBUTION OF BONDS

Qualitative analyses followed by quantitative analyses and molecular-weight determinations allow us to assign molecular formulae to organic compounds. Every organic compound has a distinct set of physical and chemical properties which differentiates it from every other compound. The physical properties most frequently used in this work include the melting point, the boiling point and interactions with light and other electromagnetic radiations. These interactions are exemplified by the refraction and absorption of light, the absorption of infra-red and ultra-violet radiation, and the rotation of the plane of plane-polarized light. Data of the type outlined above enable us to say, without fear of contradiction, that whereas, for example, there are two compounds with the molecular formula $C_2H_4Cl_2$, each of the formulae CH_4, C_2H_6 and C_2H_5Cl represents only one compound. The action of potassium cyanide on ethyl chloride (1) gives propionitrile (2) from which propionic acid (3) can be obtained by hydrolysis. The action of chlorine on this acid can give 2-chloropropionic acid (4) which, by interaction with potassium cyanide, gives 2-cyanopropionic acid (5). This compound, at sufficiently raised temperatures, evolves carbon dioxide and leaves us with propionitrile (6) which is identical in every respect with propionitrile (2) and hydrolyses to propionic acid (7) which is identical with propionic acid (3). This series of reactions does not provide us with a straight (3) and a bent (7) type of propionic acid as it could have done had the four valencies of carbon been directed towards the corners of a square.

The hydrolysis of 2-chloropropionic acid (4) gives lactic acid, $CH_3{\cdot}CH(OH){\cdot}CO_2H$, and if we proceed to prepare a number of its salts and study their recrystallization from water, we shall find, sooner or later, that the crystals provided by a particular salt are of two types, both asymmetric (since should Alice retrieve the image of any one crystal from behind the mirror it would not be superimposable on the crystal in front of the mirror) and related to one another as object to mirror image. Given great patience, good eyesight and a steady hand we can separate the crystals of one type from those of the other and thereafter recover separately the lactic acid from each. The two samples of lactic acid thus obtained have identical physical properties except in their effect on plane-polarized light. Both are *optically active*: one, named (+)-lactic acid, rotates the plane of polarization clockwise (relative to the observer) while the other, (−)-lactic acid, rotates it to exactly the same extent but anticlockwise. The ability to rotate the plane of polarized light is not lost when the two lactic acids are in solution: we conclude, therefore, that *the molecules of lactic acid are asymmetric*, a molecule of (−)-lactic acid being the mirror image of a molecule of



C_2H_5Cl (1)

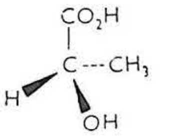
$$\rightarrow CH_3\text{—}\overset{H}{\underset{H}{C}}\text{—}CN \; (2) \rightarrow CH_3\text{—}\overset{H}{\underset{H}{C}}\text{—}CO_2H \; (3) \rightarrow CH_3\text{—}\overset{Cl}{\underset{H}{C}}\text{—}CO_2H \; (4)$$

$$\rightarrow CH_3\text{—}\overset{CN}{\underset{H}{C}}\text{—}CO_2H \; (5) \rightarrow CH_3\text{—}\overset{CN}{\underset{H}{C}}\text{—}H \; (6) \rightarrow CH_3\text{—}\overset{CO_2H}{\underset{H}{C}}\text{—}H \; (7)$$

(+)-lactic acid. That compounds of the type Ca_4, Ca_3b and Ca_2bc are unique while those, like lactic acid, of the type Cabcd can occur in (+)- and (−)-forms finds its interpretation in the concept that *the bonds attaching a carbon atom to four other atoms are directed from the centre to the four corners of a regular tetrahedron.*

CONFIGURATION

An attempt to give a three-dimensional representation of the two forms of lactic acid is shown below (8 and 10). Fischer projections provide a convenient form of three-dimensional representation (9 and 11 are the Fischer projections of 8 and 10). To obtain them, project on to the paper what an eye would see if, as it looks at the central carbon atom, the bonds directed *away from* the observer are in a *vertical plane* while those directed *towards* the observer are in a *horizontal plane.*



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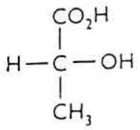
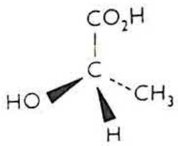


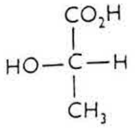
$$\begin{array}{c}\mathrm{CO_2H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{CH_3}\end{array}$$

(9)

(−) - Lactic acid



(10)



$$\begin{array}{c}\mathrm{CO_2H}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{CH_3}\end{array}$$

(11)

(+) - Lactic acid

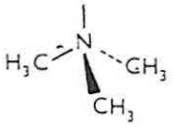
When, as in lactic acid, four different atoms or groups of atoms are attached to the same carbon atom, this atom is called an *asymmetric carbon atom*, since there are two arrangements or *configurations* of the atoms and groups attached to it. Pairs of molecules that are non-superimposable and are the mirror image of each other are called *enantiomers, enantiomorphs,* or *optical isomers.* When enantiomers are present in equal amount, the whole is optically inactive and is called a *racemate.* The lactic acid we prepared from propionic acid by chlorination followed by hydrolysis is optically inactive and is called racemic or (±)-lactic acid.

Living organisms usually produce only one enantiomer of a pair: thus the vegetable kingdom provides many optically active nitrogenous organic bases. When one of these bases, *e.g.* (−)-quinine from the bark of the cinchona tree, reacts with (±)-lactic acid, two salts are formed which can be represented by (−)-B,(+)-A and (−)-B,(−)-A in which A and B represent the acid and the base respectively. These two salts are not enantiomeric: they have the same configuration in one part and opposite configurations in the other. They are *diastereomeric.* Unlike enantiomers, *diastereomers* have different properties and, often, are conveniently separated from one another by recrystallization. Thus we can separate (−)-B,(+)-A from (−)-B,(−)-A; afterwards we can obtain (+)-lactic acid from the former and (−)-lactic acid from the latter. In this manner (±)-lactic acid has been *resolved* into its optically active enantiomers.

To discover the actual or *absolute* configuration of the lactic acid which rotates the plane of polarized light to the right and of that which rotates it to the left, we must, sooner or later, directly or indirectly, have recourse to X-ray diffraction patterns from which we can precisely deduce the spatial arrangement of the parts of a molecule. Formulae 8 and 9 represent (−)-lactic acid and formulae 10 and 11 (+)-lactic acid. The esterification of (−)-lactic acid with methyl alcohol gives the (+)-methyl ester in which the $-CO_2CH_3$ group occupies the same relative position in the molecule as does the $-CO_2H$ group in the molecule of (−)-lactic acid. Thus we are compelled to recognize that two compounds may have similar configurations yet rotate the plane of polarized light in opposite directions.

Is the 'tetrahedral distribution' of bonds shown by carbon atoms also a feature of atoms of other elements? Electron-diffraction data concerning trimethylamine (12) have shown the molecules to be pyramidal with $\mathrm{C}\overset{\mathrm{N}}{\diagup\;\diagdown}\mathrm{C}$ angles of about 108°, very nearly the same as the $\mathrm{H}\overset{\mathrm{C}}{\diagup\;\diagdown}\mathrm{H}$ angles

(109·5°) of methane molecules. We might expect to find optically active forms (13) and (14) of methylethylpropylamine, but optical isomers of this kind have not been found. Spectroscopic data show that the pyramidal molecules (13) and (14) require only about 5 kcal/mole to enable the pair of unshared electrons to pass through the nitrogen atom, and thereby invert the configuration. This amount of energy is readily available at room temperature. When the four pairs of electrons surrounding the nitrogen atom are used to bond the nitrogen atom to *four* different groups, as in methylallylphenylbenzylammonium iodide (15), two optically active forms exist. Clearly, the carbon atom is not the only one which can have its bonds directed from the centre to the corners of a regular tetrahedron, the angle between any two bonds being about 110°.



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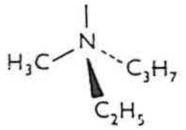

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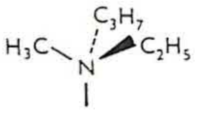

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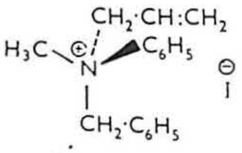
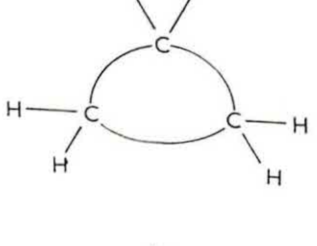


(15)

When 1,3-dichloropropane is allowed to react with zinc, cyclopropane (16) is formed.

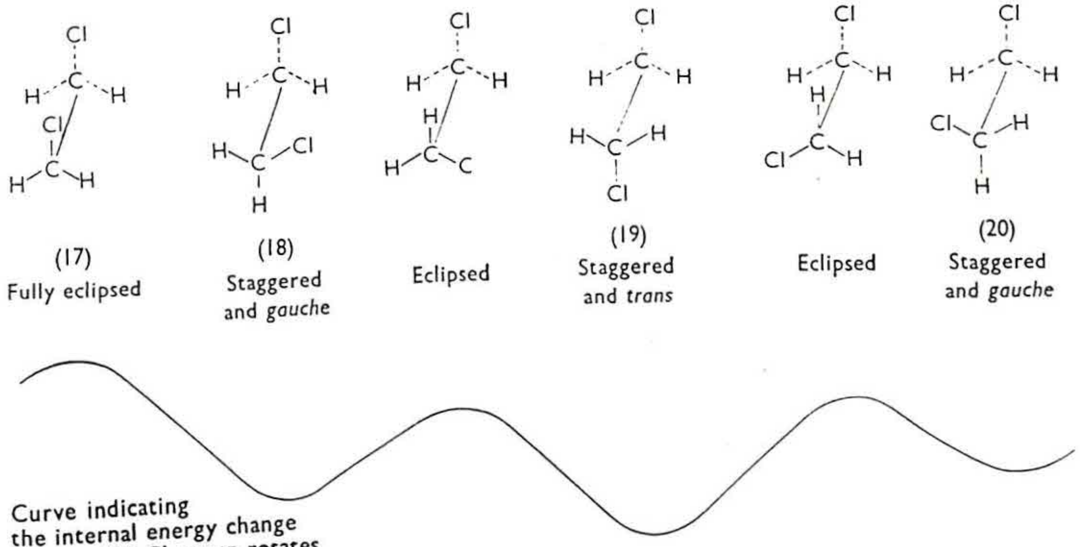


(16)

What has happened to the interbond angle of 110°? Perhaps we ought to conclude that bonds can be bent into the sausage shape shown in formula (16). From our knowledge of the molecular shapes of many compounds and of the energy, measured by infra-red spectroscopy, to change intramolecular vibrations, we are able to deduce that bonds are easier to bend than to stretch.

CONFORMATION

When we construct a model of a molecule of ethylene chloride we find that, without stretching or bending bonds, we can obtain a variety of molecular shapes by *rotating* one half of the molecule relative to the other half about the bond joining the carbon atoms. Nearly aligning our eyes with the C–C bond, let us begin with the chlorine atoms and hydrogen atoms *eclipsing* one another as shown in (17) and gradually rotate the nearer $-CH_2Cl$ group so that we pass through the shapes represented by (18), (19) and (20). Since no one has found two or more types of ethylene chloride, we might be led to suppose either that the two halves of the molecule can rotate freely and independently of one another about the C–C bond or that the molecule is restricted to one of the shapes (17) through (20). The following considerations help to resolve this ambiguity. The effects of methyl chloride on electrical fields into which it is placed show that the C–Cl bond provides an electric dipole with a moment (magnitude of the charges × distance apart) of about 2·0D, where 1D or Debye units $= 10^{-11}$ e.s.u. × Å. Ethylene chloride has two such dipoles and the dipole moment of the molecule, which can be measured, is the vector sum of the dipole moments of the two halves. If ethylene chloride were as represented by (19), its dipole moment would be zero; if as represented by (17), 3·8D. Free rotation would provide the average value of $(0 + 3{\cdot}8)/2 = 1{\cdot}9$D. Experiment reveals that its dipole moment is 1·12D at 32° and gradually increases with rise in temperature until it is 1·54D at 271°. The data are compatible with the view, now generally held, that, as one half of the molecule rotates with respect to the other (*a*) the internal energy of the molecule rises and falls as shown by the curve under formulae (17) through (20), (*b*) the molecule can rest only in the energy hollows, (*c*) the molecule prefers the hollow provided by (19) to the shallower hollows provided by (18) and (20) and (*d*) this preference becomes less apparent as the temperature is raised. The various molecular shapes (17) through (20) are called *conformations*; (19) shows the molecule in its *trans* conformation while (18) and (20) show the molecule in its *gauche* or *skew* conformations. In each of these conformations, the bonds radiating from one carbon atom are *staggered* with respect to those radiating from the other.


(17) Fully eclipsed

(18) Staggered and *gauche*

Eclipsed

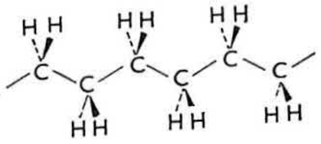
(19) Staggered and *trans*

Eclipsed

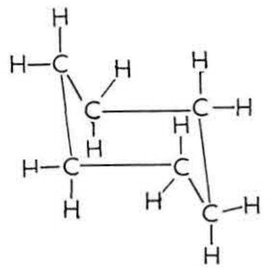
(20) Staggered and *gauche*

Curve indicating the internal energy change as one $-CH_2Cl$ group rotates

X-ray diffraction patterns produced by paraffin wax show the polymethylene chains to have the *zig-zag* conformation (21) in which every group of four consecutive methylene groups has the staggered and *trans* conformation.


(21)

When we construct a model of the cyclohexane molecule, only two conformations are possible if we are to have an interbond angle of 110°: the *chair* conformation (22) and the *boat* conformation (23). The infra-red spectrum of cyclohexane shows that at ordinary temperatures the molecules spend a much longer time in the chair than in the boat conformation. Only in the former are the bonds of each carbon atom staggered with respect to those of the neighbouring carbon atoms. The preference for staggered conformations determines molecular shape only when more important demands on shape are absent. It may originate in repulsive forces between atoms and groups, especially the bulkier ones, which are brought close together without being able to bond one to the other.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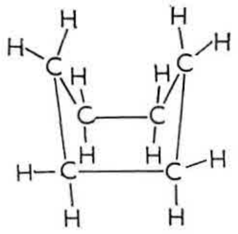
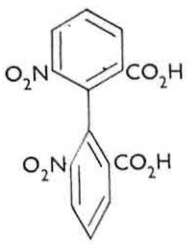

(23)

The resolution of 6,6′-dinitrodiphenic acid into its optical isomers (24) and (25) demonstrates that in this compound an amount of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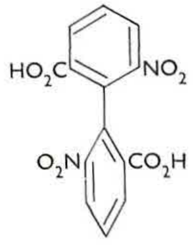
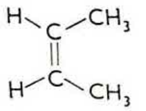

(25)

energy too large to be readily available at ordinary temperatures is required to enable the substituents in one of the rings to squeeze past those in the other. It is noteworthy that the non-planar molecules (24) and (25) are asymmetric although they do not contain an asymmetric atom.

THE COPLANARITY REQUIREMENT OF DOUBLE BONDS

When 2-bromobutane reacts with bases it can lose the elements of hydrogen bromide and give a hydrocarbon which can be separated into three components boiling at −6°, 1° and 4° severally. Each component has the molecular formula C_4H_8. The one which boils at −6° gives formaldehyde and propionaldehyde on ozonolysis and is assigned the formula $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$, while the other two give only acetaldehyde on ozonolysis and are both represented by the formula $CH_3{\cdot}CH{:}CH{\cdot}CH_3$. Of these two hydrocarbons, the one with the higher boiling point has a dipole moment and the other has not; consequently, they are given respectively the formulae (26) and (27) and named *cis*- and *trans*-2-butene. Two compounds are represented by the structure $HO_2C{\cdot}CH{:}CH{\cdot}CO_2H$; one is known as maleic and the other as fumaric acid. When heated to 140°, maleic acid gives maleic anhydride (29) and water while fumaric acid loses water to form maleic anhydride only at temperatures above 270°: consequently, they are assigned the formulae (28) and (30) respectively. Clearly, the energy barrier to rotation about a carbon-carbon double bond is sufficiently high to hold the four attached atoms or groups in a rigid configuration except at high temperatures. Electron diffraction and spectroscopic studies show ethylene to be a flat molecule with bond angles of about 120°. The isomers (26) and (27) and again (28) and (30) are called *geometric* isomers. Isomers that differ from one another only in the way the atoms are oriented in space but are identical with respect to which atoms are bonded to one another are called *stereoisomers*. Geometric isomerism and optical isomerism are both examples of stereoisomerism.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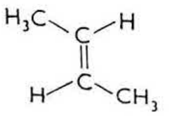
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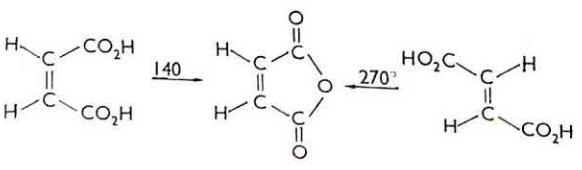
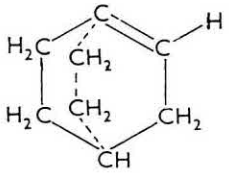


(28) (29) (30)

A carbon-to-carbon double bond requires coplanarity of the two carbon atoms and the four atoms directly attached to them (*see* 32): understandably, olefins of the type (31) cannot be obtained. Now let us turn our attention briefly to double bonds between atoms other than two carbon atoms. Although there is only one type of acetaldehyde (*see* 33), this compound condenses with hydroxylamine to give two oximes, (34) and (35). Further, *cis*- and *trans*-forms of azobenzene, (36) and (37), are well known. In the formulae (33) through (37) unshared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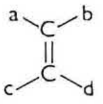
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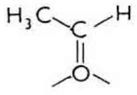
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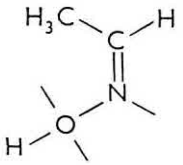
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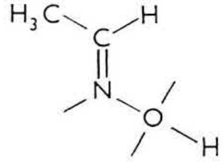
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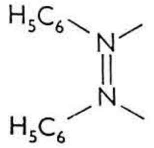
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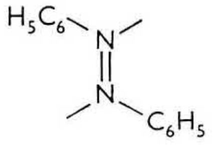
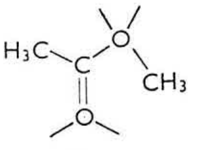

(37)

pairs of electrons, like shared pairs, are represented by lines. Clearly, a double bond between atoms imposes planarity even when the two atoms are other than carbon atoms, and is capable of providing geometric isomers when between carbon and nitrogen atoms or between two carbon or two nitrogen atoms.

CONJUGATION AND CONFORMATION

To what extent does the planarity required by a double bond determine the shape of an ester molecule? If the bonding in methyl acetate is correctly represented by (38), only the methyl group attached to an oxygen atom is free to move out of the plane of the rest of the molecule. Perhaps it is free to rotate about the bond joining its oxygen atom to the carbonyl group. The wholly planar conformations (38) and (39) represent the molecule in its least polar and most polar forms respectively. Conformation (39) should provide a dipole moment of about 4·0D, since this is the moment of γ-butyrolactone (40). Calculation leads us to expect conformation (38) to provide a moment of 1·5D. Free rotation of the methyl group through these two extreme conformations would provide an average moment of 2·7D. The measured value is 1·7D and does not change as the temperature of the ester is raised.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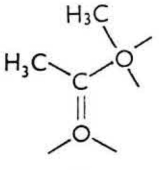
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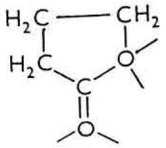
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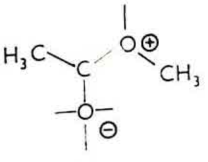
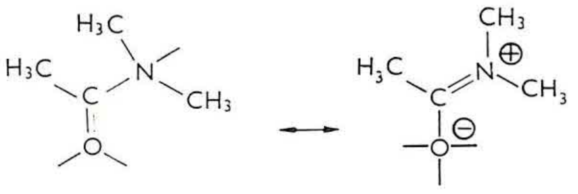
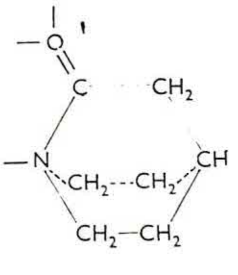

(41)

We must conclude that methyl acetate is firmly held to conformation (38). The popular interpretation of this conclusion is based on the concept that a pair of electrons, shown in (38) as belonging only to the oxygen atom of the methoxyl group, reaches to some extent into the carbon atom of the carbonyl group. This electronic redistribution, taken to 100 per cent, would result in structure (41): developed to the extent of only 10–15 per cent it would provide *partial double bonding* between methoxyl and carbonyl groups sufficient to require the methyl group of the methoxyl group to be near the plane of the rest of the molecule. This interpretation does not discriminate between conformations (38) and (39): perhaps dipole–dipole interaction of methoxyl and carbonyl groups gives preference to (38). The partial double bonding introduced above is referred to as *conjugation* or *electron delocalization*. It lowers the internal energy of any molecule in which it occurs and may require a degree of molecular planarity which is not apparent from the usual formulation. Should we fail to recognize that a molecule like acetdimethylamide (42) must have all but its hydrogen atoms close to one plane if nitrogen atom and carbonyl group are to be conjugated, we would wonder why, despite the efforts of some of the world's best chemists, the compound to be assigned the formula (43) has not been prepared (*cf.* 31).


(42)


(43)

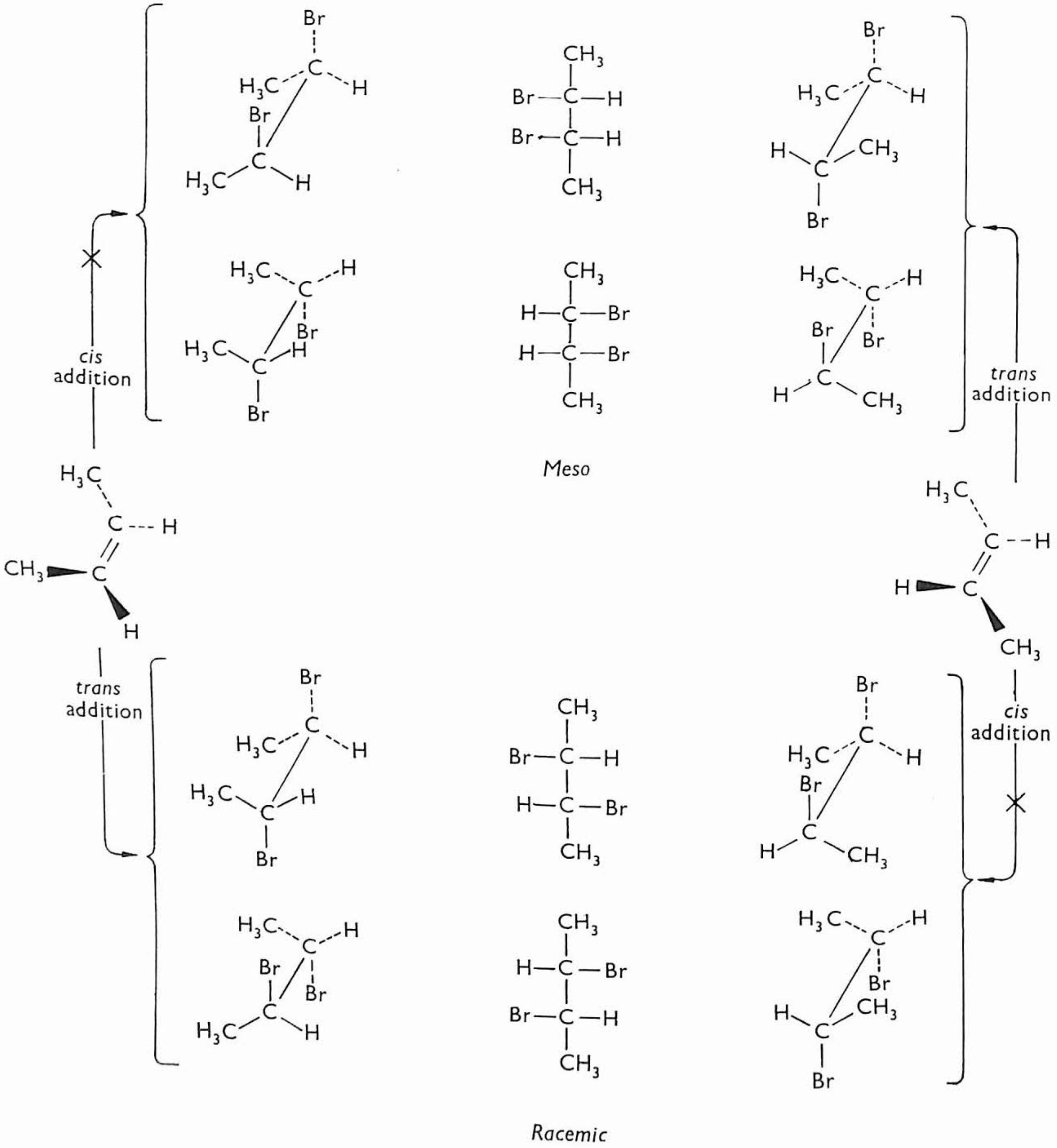
So far, this article has included very little chemistry, since it is concerned only with the shapes of molecules—a topic which these days requires no chemistry. Chemistry is concerned with processes in which bonds are changed, some being broken, others being made, and we must direct our attention to the shape requirements of some of these processes if the word 'stereochemistry' is to appear in the title of this article.

ADDITIONS TO ETHYLENIC DOUBLE BONDS

Bromine rapidly adds on to ethylene to give ethylene bromide, from which ethylene can be regenerated through the agency of zinc:

$$CH_2{:}CH_2 + Br_2 \rightarrow CH_2Br{\cdot}CH_2Br \xrightarrow{Zn} CH_2{:}CH_2$$

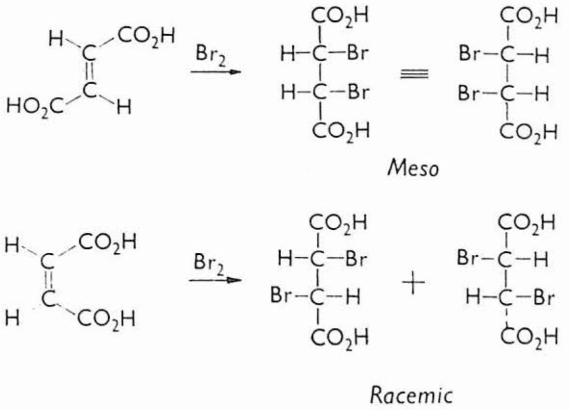
Similarly, both *cis*- and *trans*-2-butene combine rapidly with bromine to give 2,3-dibromobutane, and if zinc is allowed to react with these two samples of dibromobutane, that from *cis*-2-butene regenerates *cis*-2-butene while that from *trans*-2-butene



regenerates *trans*-2-butene. Thus we are driven to the surprising though unavoidable conclusion that the 2,3-dibromobutane from *cis*-2-butene is different from that from *trans*-2-butene. The accompanying chart shows all possible addition products of bromine with *cis*- and *trans*-2-butene. Each of the four formulae down the centre of the chart is the Fischer projection of the three-dimensional formulae which flank it. Molecular models save us much mental juggling when we try to assure ourselves that any three formulae of 2,3-dibromobutane which are side by side can be interconverted merely by rotating one half of the molecule with respect to the other half, and that all three formulae therefore represent the same molecule in different conformations. Do the four rows of formulae represent four different molecules? There are several ways of finding the answer. Let us find it by considering only the Fischer projections.

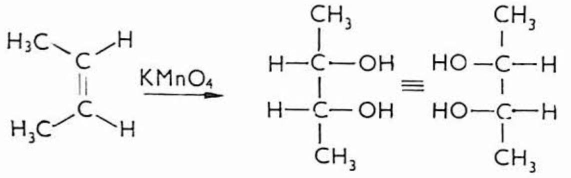
All four projections look different: do they represent four different molecules? If we turn over the lowest one, as we might turn over a hand from the palm-up to the palm-down position, it would then look like the projection immediately above it. But if a Fischer projection is to remain a Fischer projection we must not turn it over in this way, for if we do the bonds in a vertical plane will no longer be directed away from us and the bonds in horizontal planes will no longer be directed towards us. All we can do to a Fischer projection is rotate it in the plane of the paper through 180°. If we do this to the bottom two projections each retains its identity: they represent two different molecules. If we slide between them a mirror which is perpendicular to the plane of the paper we see that each is the mirror image of the other: they are optical isomers. Whether they are formed by *trans*-addition of bromine to *cis*-2-butene or *cis*-addition of bromine to *trans*-2-butene, they will be formed in equal amount: that is, *racemic* 2,3-dibromobutane will be formed. When we rotate the topmost projection through 180° it becomes the second one down: the top two projections represent the same molecule. When we place a mirror alongside these two projections we see that each is the mirror image of the other: therefore, they represent a molecule which is not asymmetric and cannot be optically active, even though it contains two asymmetric carbon atoms. They represent *meso* 2,3-dibromobutane. In the *meso* form, both halves of the molecule are asymmetric and, as shown by a vertical mirror so placed as to bisect either of its projection formulae, one half of the molecule is the mirror image of the other half. We see that 2,3-dibromobutane can occur in two optically inactive forms: the *racemic* form which is a mixture of equal parts of (+)- and (—)-2,3-dibromobutane, and the *meso* form in which all the molecules are identical and optically inactive. Meso and racemic forms are diastereomeric, since if we compare a molecule of the former with a molecule of either enantiomer of the latter we shall find the two molecules have the same configuration in one half of their molecules and opposite configurations in the other. The two different 2,3-dibromobutanes obtained by the addition of bromine to *cis*- and *trans*-2-butene must be the *racemic* and *meso* forms, but not necessarily respectively. How can we discover which form comes from *cis*-2-butene and which from *trans*-2-butene?

The addition of bromine to maleic acid gives a dibromosuccinic acid which is different from the one obtained by the addition of bromine to fumaric acid. Remembering how we resolved (±)-lactic acid with the aid of an optically active base, let us try to resolve these two dibromosuccinic acids.

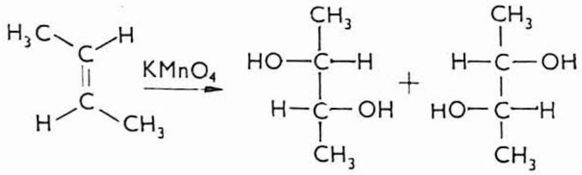


Success crowns our efforts only when we work on the one from maleic acid. Thus we learn that maleic acid gives *racemic* dibromosuccinic acid and that the *meso* dibromo acid is obtained from fumaric acid. If we are persuaded by analogy, we shall expect the addition of bromine to *cis*- and *trans*-2-butene to give *racemic* and *meso* 2,3-dibromobutane respectively. We see that the addition of bromine across an ethylenic double bond is orderly: *stereospecific* is the adjective which best describes it. The reaction is a *trans*-addition.

Another chemical property of olefins is their ability to decolorize permanganate. A glycol is formed in this reaction, a hydroxyl group having been added to each of the two carbon atoms involved in the double bond. The permanganate oxidation of *cis*- and *trans*-2-butene provides two different glycols: only the glycol from *trans*-2-butene can be resolved (I wonder how it was resolved). No doubt the reaction of olefins with permanganate leads to the *cis*-addition of two hydroxyl groups.



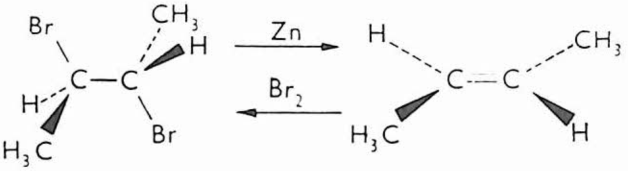
meso butan-2,3-diol



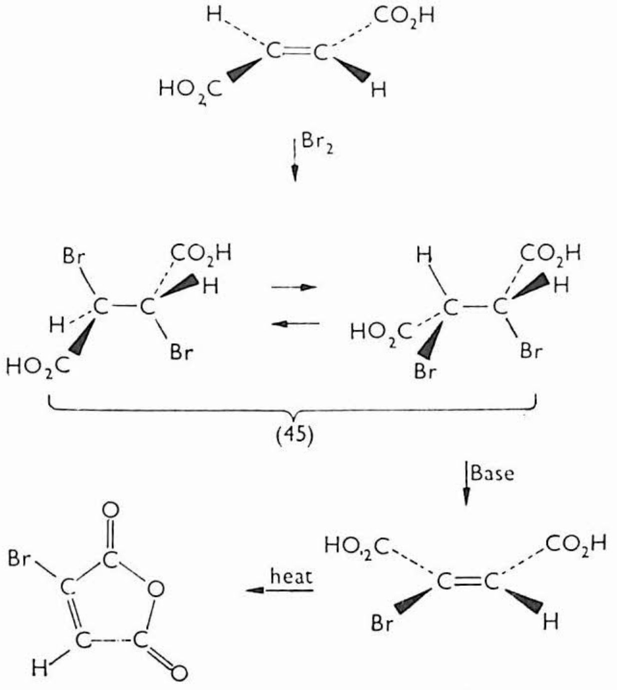
racemic butan-2,3-diol

ELIMINATION REACTIONS

Although molecules of *meso*-2,3-dibromobutane can turn from one conformation to another, one half of each molecule being able to rotate with respect to the other half, this compound reacts with zinc to give *trans*- and not *cis*-2-butene. Apparently, in this elimination process the molecule is required to have the conformation in which the bromine atoms are most widely separated: that is, the conformation in which the two bromine atoms and the two carbon atoms that link them are all in one plane and the bromine atoms are on opposite sides of the bond joining the two carbon atoms. This requirement is represented by formula (44). The reaction is stereospecific and is suitably described as a *trans*-elimination. This stereospecificity allows the reaction of *racemic* 2,3-dibromobutane with zinc to give only *cis*-2-butene.



(44)
meso-2,3-dibromobutane
trans-2-butene



(45)

(46)

Molecules which have a hydrogen atom and a halogen atom attached to adjacent carbon atoms can react with base so as to lose the elements of hydrogen halide and acquire an additional bond between the two carbon atoms. What is the stereochemistry of this elimination process?

Having already obtained *meso* dibromosuccinic acid (45) by the addition of bromine to fumaric acid, let us now, through the agency of a base, remove from it the elements of hydrogen bromide. The product readily forms an anhydride and is therefore bromomaleic acid (46).

Similarly, *racemic* dibromosuccinic acid, which we obtained by the addition of bromine to maleic acid, gives bromofumaric acid. These reactions are *trans*-eliminations: they require the hydrogen and bromine atoms which are to be eliminated and the two carbon atoms which link them to be in one plane, and the hydrogen and bromine atoms to be on opposite sides of the bond joining the two carbon atoms.

Stereochemistry is concerned with the geometry of chemical reactions, and it helps us tremendously in our attempts to discover their mechanisms. The elucidation of the mechanisms of reactions not only satisfies our curiosity; it helps us to foretell the practical procedure most likely to bring about a required reaction. Although there are numerous reactions, there are but few *types* of reaction, each defined by its stereochemistry and mechanism. The fragment of stereochemistry provided by this article is concerned with the geometry of one or two addition and elimination processes; I hope we are ready and anxious to discover the stereochemistry of other types of reactions, especially that of substitution processes, since they make a vast contribution to chemistry.

Section 5 Colour and photochemistry

Questions concerning the colours of chemical compounds must be among those most frequently received by teachers of elementary chemistry. Unfortunately, they are questions which cannot be answered simply. E. Jaffe and W. J. Marshall give an account of the colours of organic compounds and in doing so they give a very informative brief account of *s* and *p* orbitals, σ and π bonding, and elementary spectroscopy. At a more advanced level, P. A. Leermakers and G. F. Vesley present an account of the interrelation between photochemistry and electronic spectroscopy for the non-specialist in this field.

Aspects of the colour of inorganic complex compounds are covered in Cotton's article on "Ligand Field Theory" (page 90); see also R. S. Nyholm in *Chemistry To-day*, OECD, Appendix to Chapter 7.

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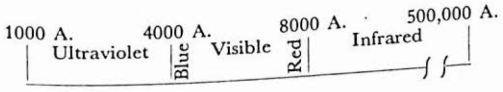
ORIGIN OF COLOUR IN ORGANIC COMPOUNDS.

E.E. Jaffe and W.J. Marshall.

Man's desire for more cheerful and esthetically pleasing surroundings, where color plays a major role, has created a vast demand for synthetic dyes and pigments. During the last century studies of the relationship between the makeup of molecules and their color have been lifted from simple empirical statements of fact to sophisticated quantum mechanical treatments. Then to this complex treatment is added another factor—color is perceived by a complicated mechanism of message relay from eye to brain. Therefore the science of color includes not only physics and chemistry, but also biology and physiology. In this article, however, only chemical and physical aspects are considered with the further limitation that only organic compounds are included.

The recent discovery that light has characteristics of both a particle and a wave has led to the conception of a light beam as a stream of particles, called photons, which in many respects behaves like a wave. All photons have the same velocity, which is the speed of light, but their energies are related to wave lengths and therefore can differ. This relationship is shown by the equation $E = 286{,}000/\lambda$, where E is energy of the photon stream in kcal. per mole of irradiated substance and λ is wave length in angstroms (A.). This expression shows that the smaller the wave length, the higher the energy of absorbed light.

Ordinary light is composed of rays having varying wave lengths, ranging from 1000 to 500,000 A., which are divided in the spectrum as follows:



This division, however, is entirely arbitrary. Nevertheless, on the basis of the above equation, it is easy to conclude that ultraviolet light has more energy, and infrared less energy than visible light.

It is visible light that produces the sensation of color, and from a physical standpoint, it can be said that color depends on the ability of objects to absorb and reflect light in the visible region of the spectrum. For example, light composed of wave lengths ranging from 4450 to 4900 A. appears blue, and if an object absorbs all light except blue, which it reflects or transmits, then the object appears blue. On the other hand, if it absorbs only blue light and transmits or reflects all other visible light, then the object appears orange, the so-called complementary color of blue. Conversely, the complement of orange is blue. When an object absorbs more than one wave length, its color, a mixture of colors complementary to those absorbed, is frequently dull.

Color of Absorbed Light Compared with Corresponding Complementary Colors

Wave Length, A.	Color of Absorbed Light	Complementary Color
4000–4200	Violet	Green-yellow
4200–4500	Indigo blue	Yellow
4450–4900	Blue	Orange
4900–5100	Blue-green	Red
5100–5300	Green	Purple
5300–5450	Green-yellow	Violet
5450–5800	Yellow	Indigo blue
5800–6300	Orange	Blue
6300–7200	Red	Blue-green

When a molecule is struck by a photon, it may absorb energy and assume what is called an energy-rich or excited state. This excited molecule then either can give up its excess energy and return to the normal or ground state, or it can undergo chemical change. When energy is given up, it is usually in the form of infrared radiation or heat, but occasionally it can be in the form of visible light known as fluorescence. Such light is usually of longer wave length and lower energy than that absorbed.

Light absorption is usually associated with the outer electrons in the molecule which are stimulated by light of specific wave lengths. If these electrons are firmly held within the molecule they respond only to light of high energy and therefore short wave length. If loosely held, they will respond to light of longer wave length and lower energy. When chemical change occurs, it is usually caused by high energy or ultraviolet rays. For organic compounds, breakage of chemical bonds (photolysis) requires energy in the range of 35 to 150 kcal. per mole, which corresponds to absorption of photons having wave lengths of 8000 to 2000 A.

Orbitals, Bonding, and Color

An electron is likely to be found in a certain region of space called an orbital, the size and shape of which depend on the electron's nature. For these orbitals shape is particularly important because it determines spatial arrangements of atoms within a molecule and influences the molecule's physical and chemical behavior. For this discussion, two general types of electrons, the *s* and *p* electrons, are considered.

The *s* electron is most likely to be found within a sphere-shaped atomic *s* orbital having as its center the nucleus of the atom. The *p* electron spends most of its time within the dumbbell-shaped atomic *p* orbital with the atomic nucleus lying between the two lobes of the dumbbell.

frequency

$E=h\nu$

Planck's Constant

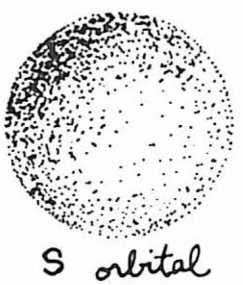
Wave length

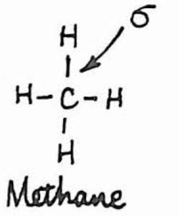
$C=\nu\lambda$

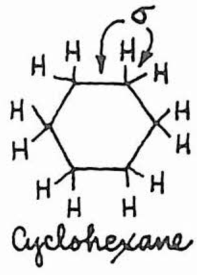
Velocity

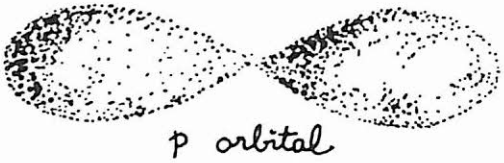
$$E=\frac{hc}{\lambda}$$

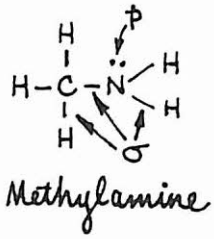
$$=\frac{286{,}000}{\lambda}$$

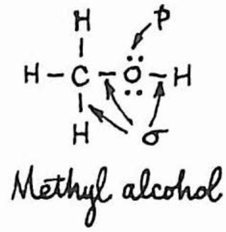




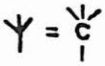








In diagrams for cyclic structures carbon atoms are at the intersection of any two bonds



In general, electrons in *s* orbitals are more stable and more tightly bound than those in *p* orbitals. When a chemical bond is formed between two atoms, the atomic orbitals overlap to form a molecular orbital.

Sigma (σ) Electrons. Bonds formed by the overlap of two *s* orbitals, an *s* and a *p* orbital, or two *p* orbitals with a common axis are referred to as σ bonds, and electrons which make up these bonds are sometimes referred to as σ electrons. For example, two *s* orbitals overlap to form the σ bond in the hydrogen molecule, whereas the σ bond in the fluorine molecule is formed by the overlap of two coaxial *p* orbitals (Figure 1).

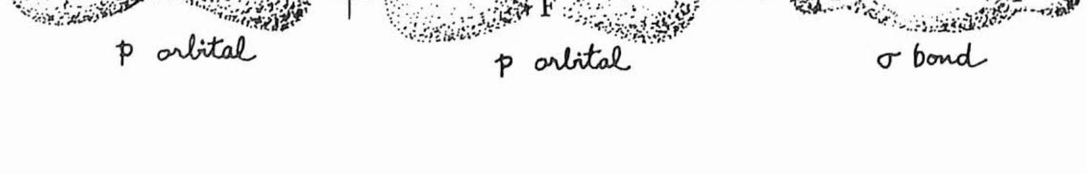
In organic molecules, σ bonds are formed by two routes: overlap of coaxial *p*-type orbitals as in the carbon-carbon bonds of cyclohexane; and overlap of *p*-type and *s* orbitals, as in the carbon-hydrogen bond of methane. It should be noted that the *p*-type orbitals in carbon are hybrids—that is, combinations of $^1/_4s$ and $^3/_4p$ orbitals, often called sp^3 hybrids.

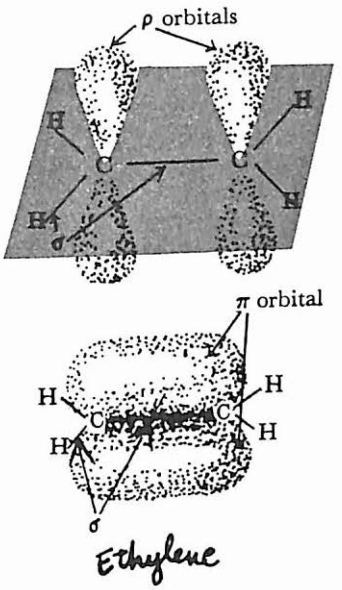
Organic compounds which contain only tightly bound σ electrons absorb in the ultraviolet high energy region of the spectrum. Examples of compounds which contain only σ bonds include methane and cyclohexane, as shown above. They absorb in the ultraviolet region below 1500 A. and are, therefore, colorless.

***p* Electrons.** Organic compounds which contain elements other than carbon and hydrogen, such as nitrogen, oxygen, and sulfur, usually possess nonbonding *p* electrons as well as σ electrons. These electrons are held less firmly than σ electrons and allow the molecule to absorb light at somewhat longer wave lengths, although still in the ultraviolet region. Examples include methylamine and methyl alcohol, as shown above.

Pi (π) Electrons. Organic compounds can also contain π bonds which are formed by the overlap of *p* orbitals with parallel axes. In ethylene—the simplest molecule containing a π bond—each carbon is bound to the other carbon and to the two hydrogens by σ bonds. These bonds utilize one *s* and two of the three available *p*-type orbitals of carbon. The remaining *p* orbital of each of the two carbon atoms has equal lobes which lie above and below the plane

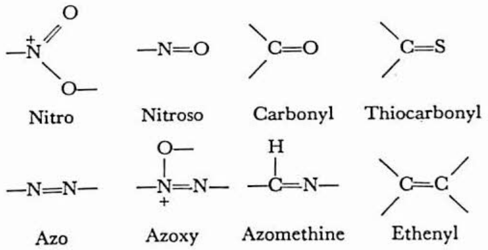
Figure 1





equal lobes which lie above and below the plane of the molecule. Overlap of these parallel *p* orbitals causes the formation of a π bond, usually designated as an additional bond between the two carbons of ethylene, $H_2C{=}CH_2$, as shown above. Electrons which make up a π bond are referred to as π electrons. Pi bonds are usually weaker than σ bonds since they are formed only when *p* orbitals are forced to be parallel by the presence of σ bonds formed from other orbitals. Pi electrons which are part of any multiple bonds or unsaturated linkages are less firmly held than σ electrons. Compounds such as ethylene, stilbene, and azobenzene, shown below, containing such linkages absorb light at wave lengths in the near ultraviolet or sometimes in the visible region of the spectrum.

Graebe and Liebermann (*1*) in 1868 recognized that color in organic compounds is associated with the presence of multiple bonds. A few years later, Witt (*4*) coined the term chromophore (from Greek chroma meaning color, and phoros meaning bearer) for groups which give rise to color. The term is now used to designate π electron groups. A series of common chromophores is listed below.



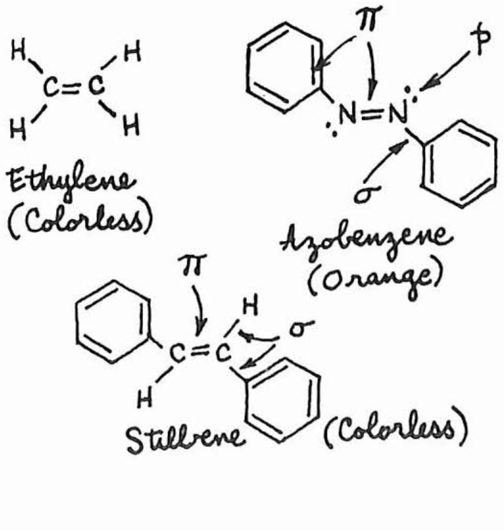
The term auxochrome (from Greek auxo meaning increase) was applied to groups which played an auxiliary role in enhancing and modifying color. The term now designates *p* electron groups. The following groups are frequently encountered auxochromes.

$—\ddot{N}R_2$	$—\ddot{N}HR$	$—\ddot{N}H_2$	$—\ddot{\underset{..}{O}}H$	$—\ddot{\underset{..}{O}}CH_3$
Dialkylamino	Alkylamino	Amino	Hydroxy	Methoxy

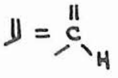
The vast majority of colored organic compounds showing selective absorption in the visible spectrum contains conjugated π electrons (double-single-double-bond sequence) referred to as π-π conjugation; in many cases π electrons conjugated with *p* electrons are referred to as *p*-π conjugation.

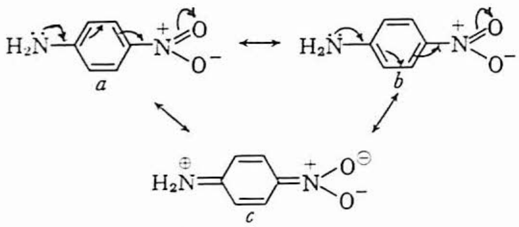
Resonance

To understand the meaning of conjugation in a broader sense and, in effect, the source of color in organic molecules, the term resonance must be understood. Resonance occurs whenever a molecule can be represented by two or more structures which contain the same number of paired electrons and differ only in the arrangement of these electrons, not in the position of its atomic nuclei. Resonance is particularly important when all or some of the contributing structures are of about the same stability, as is the case with benzene and its derivatives. For example, *p*-aminonitrobenzene, the orange substance shown in Structure I, *a*, *b*, and *c*, cannot be described adequately by one formula. It requires several formulas, three of which are shown here. This compound shows a considerable dipole moment because of charge separation, electrons having been shifted from the amino group to the nitro group, as shown by the formula with circled charges (Structure I, *c*). The present view is that *p*-aminonitrobenzene, like all colored substances, possesses a single structure at all times, which is intermediate between several formulas, including the three



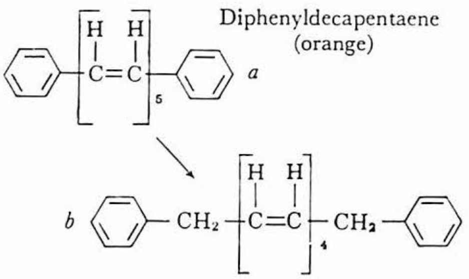
For unsaturated carbon atoms, hydrogen atoms are assumed to be attached





p-Aminonitrobenzene
(orange)

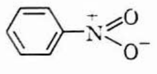
Structure I



Diphenyldecapentaene
(orange)

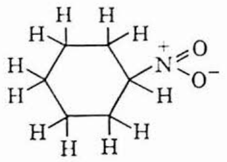
Diphenyldecatetraene
(colorless)

Structure VII



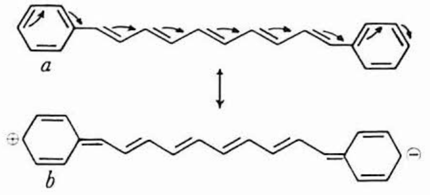
Nitrobenzene
(pale yellow)

Structure II

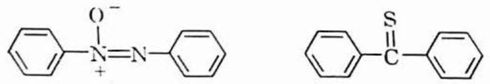


Nitrocyclohexane
(colorless)

Structure III



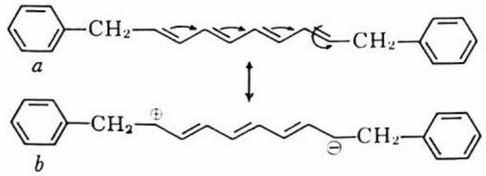
Structure VIII



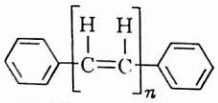
Azoxybenzene
(pale yellow)
a

Thiobenzophenone
(blue)
b

Structure IV

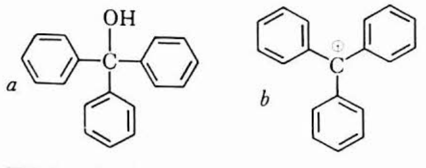


Structure IX



Diphenylpolyenes

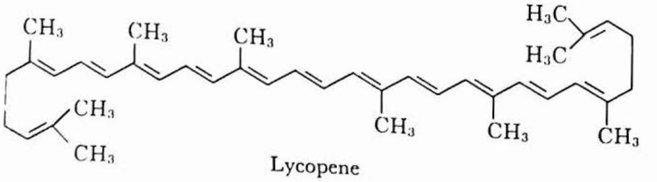
Structure V



Triphenylcarbinol

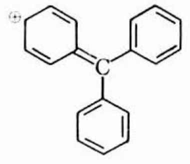
Triphenylmethyl cation

Structure X



Lycopene

Structure VI



Structure XI

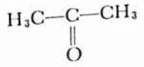
shown in Structure I, *a*, *b*, and *c*. Graphically, its structure is described by formulas in which the double-headed arrow ↔ representing resonance must be carefully distinguished from a pair of arrows ⇆ which represent a chemical equilibrium. Were it not for the resonance phenomenon which requires consideration of many structures where the amino and nitro groups are important, *p*-aminonitrobenzene would not be colored.

By removing the amino auxochrome from *p*-aminonitrobenzene and replacing it with hydrogen, light absorption of the resulting compound, nitrobenzene, is substantially diminished and shifted to shorter wave lengths. This eliminates the important contributing structure in which charge separation is shown (Structure II). However, nitrobenzene, a resonance-stabilized molecule, is pale yellow due to the nitro chromophore. If most of the resonance in nitrobenzene is eliminated by saturating the double bonds in the benzene ring with hydrogen, the color is eliminated. Nitrocyclohexane (Structure III) is a colorless compound.

The presence of resonance does not assure absorption of visible light, but most colored organic substances do exhibit resonance. In general, the larger the number of resonance structures that can be written for a compound and the closer the estimated stabilities of the individual structures, the smaller is the energy required for excitation of the molecules and the longer the wave length of light absorption.

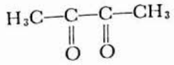
Like the nitro group, there are other chromophores which are sufficiently potent to confer color on compounds which contain only one of these groups. Thus, both azoxybenzene and thiobenzophenone are colored substances (Structure IV, *a* and *b*).

The double bonds (π electrons) in the benzene rings of the two compounds could be construed as additional chromophores, but though they do contribute to color, they are not comparable in degree of unsaturation to the olefinic double bonds (ethenyl chromophores). In most cases, more than one chromophore group must be present to give rise to color. For example, acetone is colorless, but diacetyl is yellow and 2,3,4-triketopentane is yellow-orange.



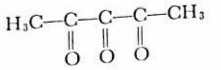
$H_3C-\underset{\underset{O}{\|}}{C}-CH_3$

Acetone
(colorless)



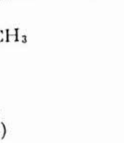
$H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$

Diacetyl
(yellow)



$H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$

2,3,4-Triketopentane
(yellow-orange)

A series of compounds, called diphenylpolyenes (Structure V), best illustrates the effect on color of increasing the number of chromophoric groups. To explain the yellow and red colors of the isomeric hydrocarbons carotene and lycopene (CHEMISTRY, February 1964, page 26), which are natural pigments found in carrots, tomatoes, and many other fruits (Structure VI), Kuhn and coworkers prepared a series of diphenylpolyenes in which *n* ranged from 1 to 7. They found that in this series of compounds an increase in the value of *n* from 2 to 3 gave rise to color, and subsequent additions of  $-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-$ caused a shift of all peaks to longer wave lengths. Throughout the series, the intensity of absorption increased quite uniformly from the first to the last compound.

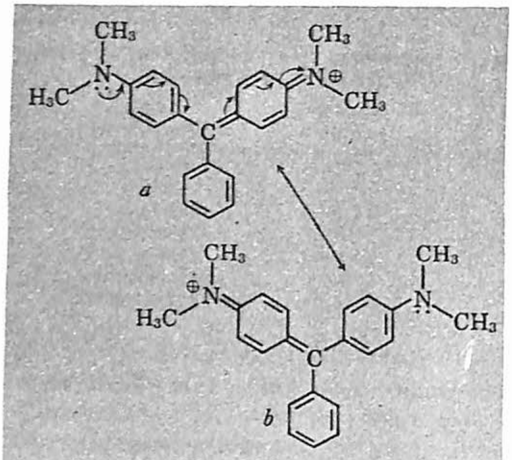
Effect of Increasing (π-π) Conjugation on Longest Wave Length Absorption (3)

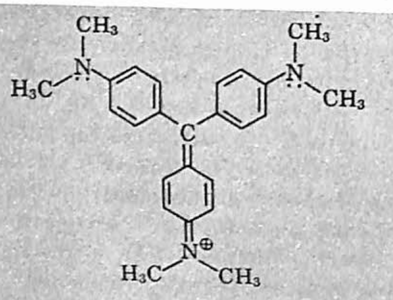
n	Wave Length of Absorption, A.	Color in Benzene Solution
1	3190	None
2	3520	None
3	3770	Pale yellow
4	4040	Green-yellow
5	4240	Orange
6	4450	Brownish orange
7	4650	Copper bronze

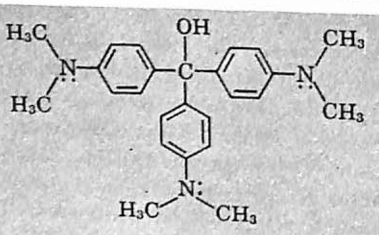
This study showed that a system of conjugated double bonds of suitable length is sufficient to confer color on long-chain hydrocarbons, a conclusion that was valuable in interpreting color in carotenoid pigments. The diphenylpolyene series of compounds differs from the natural pigments in that it contains benzene rings, so that fewer than 11 conjugated double bonds are needed in lycopene to obtain a similar color.

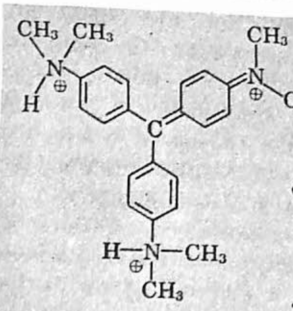
The involvement of benzene rings in the generation of color is quite important. This was shown conclusively by formation of colorless diphenyldecatetraene, the initial product obtained from the reduction of orange diphenyldecapentaene (Structure VII, *a* and *b*). The orange compound has many more contributing resonance structures than the colorless compound in which the double-single-double bond sequence has been interrupted. One contributing structure of the orange compound with extreme charge separation is shown in Structure VIII, *a* and *b*. There are many other resonance structures in which charge separation is not so distant. The number of the total contributing structures increases rapidly as the number of conjugated double bonds increases. In the colorless compound, resonance of olefinic double bonds involves fewer π electrons. This gives rise to fewer contributing structures which are insufficient for color generation. The contributing structure with the most distant charge separation is shown in Structure IX, *a* and *b*. Thus, the shorter the conjugated system, the fewer resonance structures can be written and the shorter the wave length of light absorption.

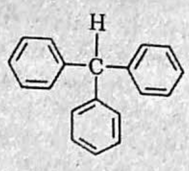
As stated earlier, auxochromes contribute to enhancement of color because their *p* electrons conjugate with the π electrons present in the molecule. This contributes additional resonance structures. For example, while triphenylcarbinol is a colorless compound and the triphenylmethyl cation formed from it in acid solution is pale colored (Structure X, *a* and *b*), introduction of auxochromes enhances the color considerably. The additional resonance structures which can be written for the unsubstituted cation, one of which is shown in Structure XI, are usually associated with absorption in the ultraviolet

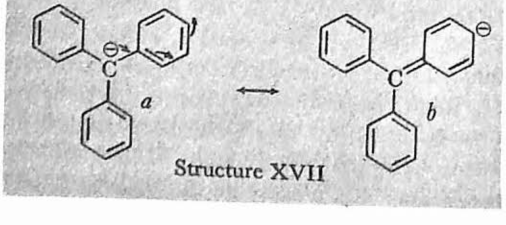

Structure XII. Malachite green


Structure XIII. Crystal violet


Structure XIV. Crystal violet base


Structure XV


Triphenylmethane
Structure XVI


Structure XVII

region of the spectrum. Introducing two auxochrome dimethylamino groups in the most distant (para) positions of two benzene rings gives rise to additional important resonance structures involving p-π (auxochrome-chromophore) conjugation. Two of many additional structures are shown in Structure XII, *a* and *b*. The compound is called malachite green because it resembles the color of the copper ore malachite. It imparts a beautiful blue-green color to wool and silk.

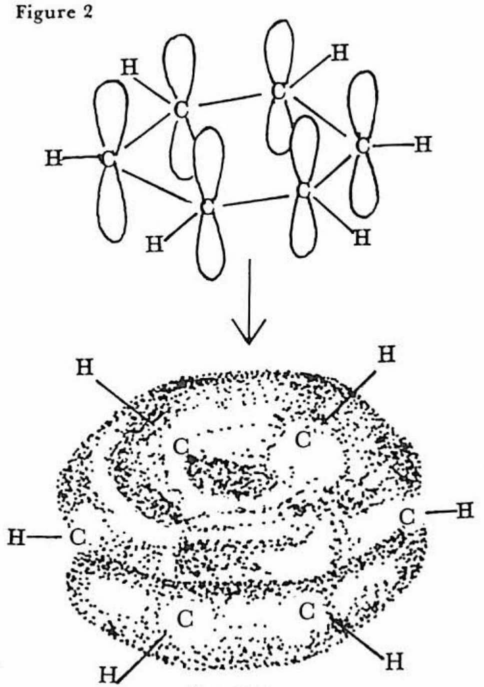
By introducing a third dimethylamino group into the third benzene ring, more structures can be written. Crystal violet, an important one, is shown in Structure XIII. Crystal violet is an excellent dye for silk and wool. As in malachite green, resonance distributes the positive charge over many atoms and 56 different resonance structures can be written. However, resonance is highly impaired when the positive charge is either removed or immobilized. Thus treatment of crystal violet with base gives rise to the colorless compound, crystal violet base (Structure XIV). Likewise, on treatment with a sufficient amount of acid, a colorless trication is obtained in which the positive charges are immobilized (Structure XV) because the p electrons of the nitrogens are involved in bonding and therefore are not available for conjugation with the π electron system.

To create color, it is not necessary that the charge be positive because resonance can occur equally well in an anion. Triphenylmethane, a colorless compound (Structure XVI) can be converted by reaction with base to an orange triphenylmethyl anion, the structure of which can be described accurately only by many formulas, two of which are shown in Structure XVII, *a* and *b*. The acid base indicator phenolphthalein and the dye eosin belong to this general class of compounds.

Molecular Orbital Method

All colored compounds which have been considered have one important feature in common—they exhibit the phenomenon of resonance. Several theories have been advanced to explain the relationship between resonance in organic molecules and absorption of light in the visible spectrum. Based on such theories, attempts have been made to correlate structure with color. However, not until the advent of quantum mechanics and the development of the molecular orbital method for numerical calculations of resonance energies, was it possible to calculate and predict spectra and, consequently, color of certain compounds. In this method, the elec-

Figure 2



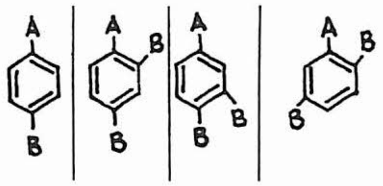
Benzene

tronic configuration of a molecule is treated as an electronic cloud around the molecule rather than as individual electrons shared by atoms.

To illustrate: In the planar benzene molecule, the p orbital of any of the six carbon atoms not used in σ bonding overlaps with the p orbital of an adjacent carbon to form a π bond—as in the ethylene molecule described earlier. Because of the symmetrical arrangement of the atoms, however, each p orbital can overlap as much with a p orbital of a neighboring carbon on one side as on the other. The addition of all six atomic p orbitals gives a molecular orbital which is continuous about the entire ring and which resembles two somewhat bumpy doughnuts (Figure 2), one on each side of the plane of the atomic nuclei.

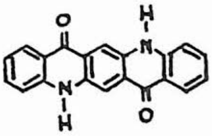
Considering all necessary molecular orbitals to which the six π electrons of the benzene system are assigned, it is possible to obtain an overall electron distribution. When substituents—for example, auxochromes—are attached to the benzene ring, their p orbitals become part of the molecular orbitals of the system. Details of this treatment are beyond the scope of this article, but the results of one study (*2*) involving aromatic systems are described below.

For the following imaginary compounds in which *A* is a chromophore and *B* an auxochrome, the wave length of major light absorption was calculated and compared with measured light absorption of the series of compounds in which $A = NO_2$ and $B = NH_2$.

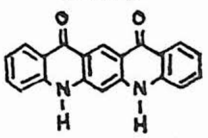


Angstrom, calculated	3200	3700	4200	5000
Angstrom, measured	3720	3860	4080	4700

Agreement, though quantitatively inexact, is remarkable in view of the fact that the calculations were carried out for a pair of imaginary groups for which certain reasonable values were assumed for the required parameters or constants. The same authors have made calculations which can be indirectly used in comparison of the colors of the following two isomeric compounds shown at the right.



Quinacridone (Red)



Isoquinacridone (Yellow)

The calculations predict that the first compound should absorb light at longer wave lengths than the second compound and the difference in wave lengths of their major absorptions should be approximately 1100 A. The two compounds are in fact red and yellow pigments, respectively.

This approach holds much promise for future calculations of spectra and, consequently, the prediction of color for many known and as yet unknown colored organic compounds.

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(4) Witt, O. N., *Ibid.*, **9**, 522 (1876).

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Organic Photochemistry and the Excited State

It has been known for well over one hundred years that organic molecules may be transformed by ultraviolet and visible light, but for most of the last 50 years the science of photochemistry has resided mainly in the realm of the physical chemist. Relatively simple systems were studied, and often the emphasis was on secondary free radical processes rather than on the primary photochemical process. In the last few years, however, the scope of the field has expanded tremendously, as manifested by the numerous reviews on the subject (*1–8*).

There are several reasons for the recent interest in photochemistry. The two major ones probably are: the absorption of photons having a specific selected energy can accomplish syntheses which may be difficult or impossible by conventional (thermal) methods, and there is rapidly growing interest in the theory of the relationship between the nature of the excited state of a molecule and its photochemical behavior. This paper will primarily deal with the latter subject.

In essence, the science of photochemistry is the detailed history of a molecule, from the time absorption of a photon raises it to an excited state from its ground state to the time it returns to its ground state or until products derived from it become stable species in their ground states. A photochemical reaction is any chemical reaction initiated by ultraviolet or visible radiation. It is obvious that for a photochemical reaction to occur, light must be absorbed by some molecule in the system, and hence this molecule must possess an absorption band corresponding to the wavelength of the incident light.

Elementary Spectroscopic Concepts (*9-22*)

An organic molecule in which all of the electrons are in "stable orbitals" and are paired is said to be in the ground singlet state, S_g. The stable orbitals will be bonding molecular orbitals, and may also be nonbonding atomic orbitals if heteroatoms such as nitrogen or oxygen are in the system. When a photon is absorbed by the molecule, one of the electrons in a bonding or nonbonding orbital is excited to an unoccupied orbital of higher energy—an antibonding molecular orbital. Since spin must be conserved in this process or transition (see below), the excited state so produced will be an upper singlet state, S_n, with all electronic spins still paired, and multiplicity still equal to one.[1] The initially excited molecule may find itself in any of the allowed vibrational levels of the S_n electronic excited state, but very rapidly, in the order of 10^{-13} sec, it decays to the lowest vibrational level of the S_n state. If S_n is a higher energy state than the lowest or first *excited* singlet state (i.e., $n > 1$), it will quickly decay nonradiatively by a process called *internal conversion* in the order of 10^{-11} sec to the S_1 state, which now possesses a longer lifetime of 10^{-8} to 10^{-7} sec. As implied by the notation, the multiplicity has remained the same.

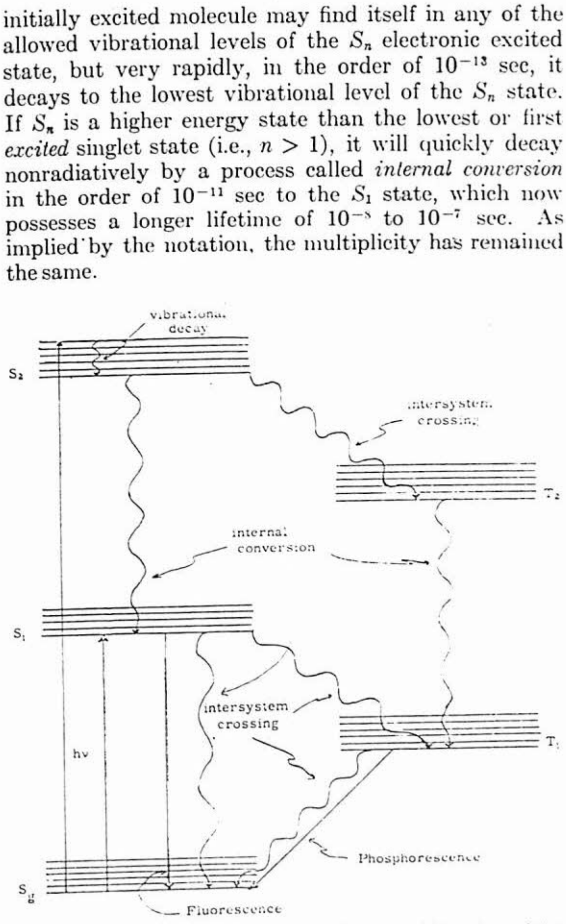

Figure 1. Straight lines indicate absorption or emission of a photon; wavy lines indicate nonradiative transitions.

At this point the generality in the spectroscopic history of organic molecules in condensed phases vanishes, and a number of paths are available for the decay of the S_1 state—depending upon the nature of the molecule, the temperature, and the physical state. Figure 1, known as a Jablonski Diagram, illustrates these paths. A molecule in the S_1 state may return directly to the ground state by emission of a photon (a radiative process) called fluorescence, or by internal conversion, the nonradiative process in which the energy is thermally dissipated to the surrounding molecules. In either case the initially promoted electron simply returns from the antibonding orbital to the bonding or nonbonding orbital whence it came with no change in spin.

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[1] The spin, S, of an electron is $\pm 1/2$. The multiplicity of a system is given by the formula $2|S| + 1$. For a singlet with all spins paired the total spin is zero. Therefore the multiplicity $2|S| + 1 = 1$. Should two electron spins become unpaired, and net spin $= \pm 1$, then the multiplicity $2|S| + 1 = 3$, and the state is said to be a triplet (T) (*23*).

The molecule in the S_1 state may also undergo chemical reaction such as decomposition, isomerization, or rearrangement. More about specific chemical reactions will be considered later. In addition, the molecule, by a process known as excitation transfer, may revert directly to the ground state and excite a neighboring molecule to an electronically excited singlet state of equal or lower energy. A final possibility of great interest is that the molecule in the S_1 state can undergo a nonradiative process called *intersystem crossing* to the *triplet state*. The triplet state has a net spin of one and hence a multiplicity of three. Intersystem crossing is "formally forbidden" because it involves a change in electronic spin (the spin of the promoted electron may be thought of as having been inverted), but it occurs with an amazingly high efficiency, in the order of 10^{-9} sec, in certain organic molecules, most notably many aromatic and carbonyl-containing compounds. For each *excited* singlet state (i.e., S_1, S_2, S_3) there is a corresponding triplet state (T_1, T_2, T_3) with two electrons with spins unpaired. The triplet is always of lower energy than the corresponding singlet. This situation is covered by the generalization known as "Hund's first rule" (*24*) which states that a system of highest multiplicity will have the lowest energy. This may be naively visualized by considering that if the spin of the promoted electron is no longer paired with its original partner (i.e., the spins are now in the same direction), the electrons cannot get very close to each other in space without violating the Pauli Exclusion Principle. Thus interelectronic repulsion is minimized, and the energy of the system is correspondingly lowered. If a higher triplet (T_2, T_3, etc.) is formed by intersystem crossing, which would happen if T_2 is lower in energy than S_1, or, improbably, if S_2 or some higher initially excited singlet excited state underwent intersystem crossing *faster* than internal conversion, this triplet will undergo rapid internal conversion to the lowest triplet T_1.

Since a molecule in the S_1 excited state has a number of paths open to it, so also does a molecule in the T_1 state. The point to be stressed here is that the T_1 state has a *much longer lifetime* than the S_1 state—by a factor of a million or more. This is because the molecule in the lowest triplet state cannot return to the ground state without inversion of an electronic spin (the ground state is a singlet). Since any transition to the ground state will be *formally* forbidden, the molecule may potentially remain in the T_1 state for a considerable time, even as long as a second in extreme cases. Ultimately, of course, the excited triplet molecule does dissipate its energy both by radiative and nonradiative paths. The T_1-S_0 radiative transition is known as *phosphorescence* (usually observed only at low temperatures such as that of liquid nitrogen). The photon emitted has lower energy than that in S_1-S_0 fluorescence, and thus the luminescence appears at correspondingly longer wavelengths.[2]

The nonradiative paths are (*a*) simple thermal decay to the ground state, this process being in a sense a combination of intersystem crossing and internal conversion, (*b*) photochemical reaction to yield a new molecule, and (*c*) energy transfer to a neighboring molecule so that the latter in turn is excited to a triplet state of equal or lower energy. If the T_1 state of the neighbor (and potential acceptor) is higher in energy than the T_1 energy of the donor, the excitation transfer will, of course, not occur. A fascinating new area of photochemistry is the study of the chemical reactions taking place in the acceptor molecule after it has been "sensitized" or energized by the triplet donor. This subject will be discussed later in some detail.

Types of Electronic Transitions

Thus far the discussion has centered around the multiplicity and lifetimes of excited states, without regard to the actual electronic structure of the excited state. To the organic chemist there are two important kinds of electronic transitions leading from the ground to an excited singlet (and perhaps then to a triplet) state that occur in the accessible region of the ultraviolet. These are known as π-π^* and n-π^* transitions,

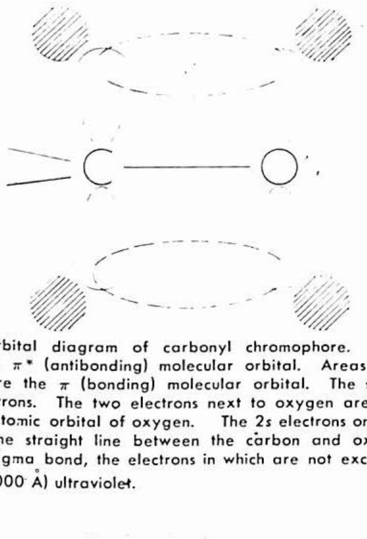

Figure 2. Orbital diagram of carbonyl chromophore. The shaded areas are the π^* (antibonding) molecular orbital. Areas enclosed in dotted lines are the π (bonding) molecular orbital. The small arrows represent electrons. The two electrons next to oxygen are in the nonbonding $2p_y$ atomic orbital of oxygen. The 2*s* electrons on oxygen are not shown. The straight line between the carbon and oxygen atoms represents a sigma bond, the electrons in which are not excitable in the near (2000–4000 Å) ultraviolet.

and the corresponding excited states so produced are known as π-π^* and n-π^* states. Consider a simple carbonyl compound (where the S_1 state is usually n-π^* and S_2 is π-π^*) which has, in the ground state, two electrons in the bonding π orbital of the C=O double bond and two electrons in the nonbonding p_y orbital on oxygen (Fig. 2). Promotion of one of the electrons shown to the π^* antibonding orbital will give rise to an excited state. If the electron is promoted from the $2p_y$ nonbonding orbital on oxygen the transition is designated n-π^*, whereas if the electron arises from the π bonding orbital, the transition (and resultant excited state) is known as π-π^*. Since the decay (internal conversion) from the higher energy to the lower energy state is very fast, it is obvious that the kind of excited state which is lowest will play a significant role in the photochemistry of the molecule. The n-π^* state has a good deal of free radical character on oxygen due to the lone electron left in the p_y orbital, but the π-π^*

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[2] The phosphorescence spectrum of a molecule is the most convenient source of information concerning its triplet energy level. The wavelength of the emitted photon may be directly related to its energy, which will be the difference in energy between the T_1 and ground states. Lewis and Kasha (*25*) were the first workers to identify the phosphorescence spectrum of an organic molecule as $T_1 - S_0$ radiative emission.

state does not We will see later how this fact affects the photochemistry of various carbonyl compounds. In general n-π^* transitions are characterized by low intensity ($\epsilon < 200$), the maximum is shifted toward the blue in hydrogen bonding solvents (the p_y electrons become "hydrogen bonded" and require more energy for their excitation), and the transition may vanish completely in strong acid media. A π-π^* transition is usually of much higher intensity, and shows a much smaller solvent dependence—in the opposite direction; i.e., the maximum shifts slightly toward the red as the medium becomes more polar.

Transition Probability

The transition probability is a measure of the probability that a photon, possessing the appropriate energy (i.e., of the right wavelength), rather than passing directly through a molecule, will be absorbed causing an electronic transition. The oscillator strength (f) is a measure of the transition probability, and will vary between zero and one depending upon the molecule and transition involved. The oscillator strength may be found from the relation:

$$f = 4.319 \times 10^{-9} \int \epsilon \, d\nu$$

where ϵ is the molar extinction coefficient at the maximum of the absorption band, and ν is frequency in cm^{-1}. The coefficient before the integral is essentially a normalization factor, and f is unitless. The oscillator strength is related to the mean radiative lifetime of the excited state by the approximate expression:

$$f = \frac{1.500}{\bar{\nu}^{2} \tau}$$

where $\bar{\nu}$ is absorption maximum in cm^{-1} and τ is the mean lifetime. As one can see, as the probability of a transition increases as manifested by increasing f or ϵ, the lifetime will correspondingly decrease. Transitions will not be allowed (f will be very small) if there is no spatial overlap of the orbitals in which the promoted electron resides in the ground and in the excited state, if spin is not conserved, i.e., a change in multiplicity occurs, and if certain symmetry requirements are not fulfilled.

Energy Transfer

As mentioned earlier, an excited molecule in the S_1 or T_1 state can, along with other possible paths of decay, transfer its excitation to a neighboring molecule, thereby exciting the acceptor to an electronically excited state of equal or lower energy. If D is the donor or sensitizer, and A is the acceptor, the process may be written:

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{D}^*$$

$$\mathrm{D}^* + \mathrm{A} \rightarrow \mathrm{D} + \mathrm{A}^*$$

$$\mathrm{A}^* \rightarrow \mathrm{A} + h\nu$$

$$\mathrm{A}^* \rightarrow \mathrm{A} + \text{heat}$$

$$\mathrm{A}^* \rightarrow \text{products}$$

The transfer of singlet excitation, observable by studies of induced fluorescence, has been established for some time (*14*). Forster (*15*) proposed a theory of long range singlet-singlet energy transfer arising from coupling of the transition dipoles of sensitizer and acceptor molecules. This theory requires that there be some overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor, even though the process is not a radiative emission-absorption phenomenon.

Of more use chemically, and of great intrinsic interest, is the phenomenon of triplet-triplet energy transfer. This is not a long range effect, but does appear to occur upon every collision of a donor with an acceptor of lower triplet energy (*26*). The process may be thought of as a coupled transition, which should have no spin restriction and thus be perfectly allowed since the net multiplicity of the donor-acceptor system does not change. Figure 3 schematically represents the process.

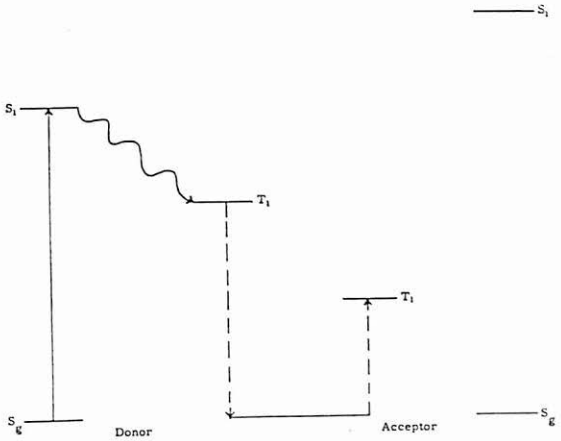
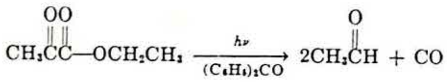


Figure 3. Energy diagram for triplet excitation transfer. Solid line represents radiative absorption, wavy line intersystem crossing, dotted line the coupled *T-T* transition. Note that the acceptor singlet states are not involved.

Terenin and Ermolaev (*27–29*) were the first investigators to report triplet-triplet energy transfer by their observation of induced phosphorescence at 77°K in a rigid matrix. By selectively exciting sensitizers such as benzophenone or benzaldehyde, both of which undergo efficient intersystem crossing, in the presence of relatively high concentrations of naphthalene (which has a lower energy T_1 state but higher energy S_1 state than the two benzoyl compounds), they found phosphorescent emission from the carbonyl compounds *and* naphthalene. Where naphthalene had been a nearest neighbor to a benzophenone (or benzaldehyde), apparently energy transfer occurred with the resulting emission of a photon from the quencher (acceptor). Backstrom and Sandros (*30, 31*) shortly thereafter observed induced phosphorescence of biacetyl in solution, and since 1961 numerous workers have employed sensitizers (triplet donors) in solution in order to effect an easy method for obtaining triplet states of molecules where intersystem crossing is very inefficient or does not occur at all, to put energy into molecules whose S_1 states are too high in energy to excite conveniently with available light sources, and to obtain triplet states of molecules where the singlet is too chemically reactive to have time to undergo intersystem crossing. The value of triplet-triplet energy transfer as a synthetic tool has been enormous.

Rather than attempt to cover extensively the field of sensitized or triplet donor-induced chemical reactions, we shall limit ourselves to specific illustrative examples in several general areas.

Sensitized Photodecompositions. Ethyl pyruvate, although decomposing relatively efficiently by direct irradiation, has been found to decompose nearly twice as efficiently in the presence of benzophenone (32).



$$CH_3\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}{-}OCH_2CH_3 \xrightarrow[(C_6H_5)_2CO]{h\nu} 2CH_3\overset{O}{\overset{\|}{C}}H + CO$$

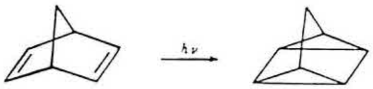
In the latter case virtually all of the light was absorbed by benzophenone; thus if energy transfer were not occurring, no reaction at all would ensue. The fact that benzophenone undergoes exceedingly efficient intersystem crossing indicates that it is triplet excitation being transferred. Another example of sensitized decomposition is found in the case of diazomethane, a compound that readily decomposes by direct irradiation to yield methylene and nitrogen.

$$CH_2{=}N{=}N \xrightarrow[(C_6H_5)_2CO]{h\nu} CH_2\!: + N_2$$

Energy transfer from benzophenone leads to the same fragments, but the electronic spins in the carbene thus produced are in this case unpaired (*33*). The difference between triplet and singlet methylene is manifested by different chemical behavior.

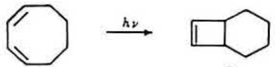
Sensitized Olefin Isomerization. It has been known for a considerable period of time that direct irradiation can effect the cis-trans isomerization of olefins. However, it has relatively recently been found that triplet donors can effect the isomerization of 2-butene (*34*), 2-pentene and 1,3-pentadiene (*35*), the stilbenes (*36*), and others. In the latter two cases there is an interesting dependence of the cis to trans ratio in the "photoequilibrated" mixture on the triplet state energy of the sensitizer. As an example, in the case of the 1,3-pentadienes, the mixture becomes increasingly rich in the trans isomer as the triplet energy of the sensitizer is lowered (as one goes from benzophenone to acetylnaphthalene, for instance). As the donor triplet energy is further reduced, a point is reached (55 kcal) where isomerization no longer occurs. This has been explained on the basis that the cis pentadiene triplet lies lower in energy than the trans; thus as the donor energy becomes increasingly lower, it begins to selectively donate excitation to the cis since transfer to the trans will begin to become endothermic. Even though the cis and trans triplets both decay about evenly to cis and trans ground state molecules, selective excitation of the cis will eventualy lead to a "photoequilibrated" mixture rich in trans. When the donor energy goes below the cis pentadiene triplet energy, no isomerization at all occurs.

Sensitized Olefin Dimerization and Ring Closure Reactions. This area represents the greatest synthetic utilization of triplet energy transfer. A most dramatic example of ring closure is found in the transformation of norbornadiene to quadricyclene.



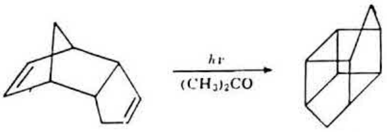
Dauben and Cargil (*37*) found that direct irradiation of norbornadiene at 2050 Å led to the ring-closed product slowly and in relatively low yield. However, Hammond, Turro, and Fischer (*38*) found that irradiation of the diene at 3130 Å in the presence of acetophenone as sensitizer led to the formation of quadricyclene in 95% yield. Since singlet-singlet transfer to the diene from acetophenone is energetically impossible, the triplets of the two molecules probably lie fairly close together and acetophenone can and does act as a triplet donor.

Direct irradiation of 1,3-cyclooctadiene for long periods of time produces the bicyclic structure I (*39*).



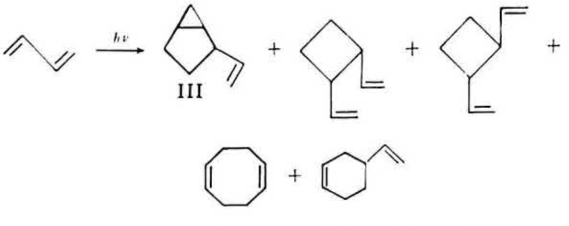
I

The same result may be obtained more rapidly by utilizing benzophenone as a sensitizer (*4*). In some cases utilization of a sensitizer is the only way in which closure may be carried out. *Endo*-dicyclopentadiene shows no cycloisomerization upon direct irradiation, but in the presence of a sensitizer (acetone in this case) good yields of the caged compound II are obtained (*40*).



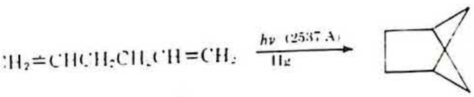
II

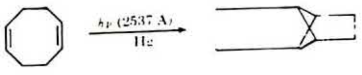
Photodimerization of butadiene has been studied in the absence and presence of triplet donors. Although purely thermal dimerization yields primarily 4-vinylcyclohexene (*41*), about 4% *trans*-divinylcyclobutane with traces of octa-1,3,7-triene (*42*), direct irradiation of 1,3-butadiene yields seven dimers, the principal ones being shown below. The major product is 2-vinylbicylo-[3.1.0]-hexane III (*43*).



Photosensitized dimerization of butadiene yields only three dimers (*38, 44*) *cis*- and *trans*-1,2-divinylcyclobutane and 4-vinylcyclohexene, the ratio of products being dependent on the sensitizer used. Numerous other examples of sensitized olefin dimerizations have appeared recently in the literature, but will not be discussed here.

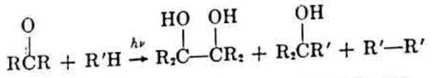
Energy transfer from an inorganic species, triplet mercury atoms (in the vapor phase), has recently been utilized by Srinivasan to carry out the following interesting transformations (*45, 46*):





The Nature of the Excited State and Photochemical Reactivity

Photoreduction of ketones (and aldehydes) in the presence of hydrogen donors,



$$R\overset{O}{\overset{|}{C}}R + R'H \xrightarrow{h\nu} R_2\overset{HO}{\overset{|}{C}}—\overset{OH}{\overset{|}{C}}R_2 + R_2\overset{OH}{\overset{|}{C}}R' + R'—R'$$

is a well known photochemical process (*47–49*). Prior to 1960 the literature dealt with the chemical mechanism—hydrogen atom abstraction by the excited carbonyl onto oxygen leaving a dialkyl (or diaryl) hydroxymethyl radical along with the radical derived from the hydrogen donor molecule. Subsequent coupling of identical radicals yields the pinacol and the dimer derived from the hydrogen source. Cross coupling (coupling of the two different radicals) also occurs.

There has been much recent interest in the multiplicity and nature of the chemically active excited state involved in photoreduction reactions. The results will be discussed in some detail since the information obtained is exceedingly pertinent to the theme of this paper.

Hammond and co-workers (*50*) and Backstrom (*30*) deduced that the chemically active excited state responsible for photoreduction of benzophenone and presumably other ketones as well is the triplet. Hammond's original argument was based on considerations of lifetime (the singlet would be too short-lived to seek out a hydrogen donor), and was further strengthened by the fact that paramagnetic species which deactivate triplet states and species with lower-lying triplets, which would act as excitation acceptors thus deactivating triplet benzophenone, markedly reduced the efficiency of the photoreduction. Phosphorescence studies at 77°K (*51*) had previously indicated that intersystem crossing in benzophenone was extremely efficient, thus the result was perhaps not too surprising.

The question now arises as to the nature of the excited triplet involved in the photoreduction, i.e., is the state n-π^* or π-π^*? On the basis of phosphorescence and other data, it is felt that the lowest and hence chemically active triplet of benzophenone and other ketones that undergo facile photoreduction is n-π^*. This is inherently reasonable, since as we have already seen the n-π^* transition involves promotion and hence removal of an electron in a nonbonding p orbital on oxygen leaving a single odd electron to occupy the orbital. This gives the oxygen atom considerable free radical character enabling it to abstract radical hydrogen rather easily, especially so when one considers the higher energy of the O—H bond formed in relation to the energy of the C—H bond broken in the hydrogen donor (an ether, secondary alcohol, many hydrocarbons, but not benzene).

It has, however, been found that certain carbonyl compounds such as 2-acetylnaphthalene and 1-naphthaldehyde (*52*) and several substituted benzophenones (*53*) are extremely inert to photoreduction, even by exceptionally good hydrogen donors. Only tri-*n*-butylstannane, with an exceedingly weak Sn—H bond (and thus, perhaps, one of the best known sources of radical hydrogen) could effect photoreduction of the naphthoyl compounds. Hammond and Leermakers (*52*) and Pitts (*53*) each proposed that the reason for inefficient photoreduction of the above compounds was that for these molecules the lowest triplet state was π-π^* rather than n-π^*. Phosphorescence data on these compounds seemed to confirm this proposal. Although in unsubstituted benzophenone the carbonyl group is conjugated with the phenyl groups, and the lowest triplet is n-π^*, the extra conjugation found in the naphthoyl compounds and certain substituted benzophenones alters the energy levels of the excited states such that the lowest triplet in these cases is π-π^* rather than n-π^* (Fig. 4). As can be seen from Figure 4, the fact that the lowest excited singlet (S_1) may be n-π^* does not necessarily mean that the T_1 state is also n-π^*. In general S-T energy differences between n-π^* states are considerably less than S-T energy differences for π-π^* states. Thus if there is a π-π^* singlet state very close to the n-π^* singlet, the lowest, and hence chemically active, triplet will be π-π^*. In the unreactive carbonyl compounds mentioned, where the lowest triplet is π-π^*, there is no free radical character on oxygen and the excitation is delocalized throughout the molecule. Thus for photoreduction to occur, considerable activation energy would be required for the electronic reorganization in the excited state necessary to make the oxygen attractive for hydrogen atom transfer from the hydrogen donor.

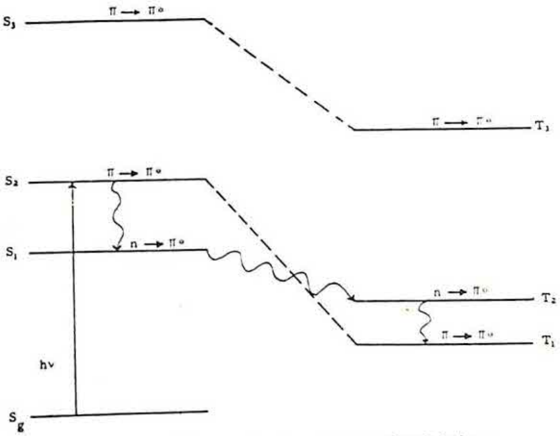


Figure 4. Energy levels for a molecule such as acetylnaphthalene.

Another example of the dependence of photochemical reactivity on the nature of the excited state is found in the photolysis of α-keto esters (*54*). Ethyl, methyl, and isopropyl pyruvate photodecarbonylate relatively readily in benzene solution with quantum yields[3] of the order of 0.16. Ethyl naphthoylformate, IV,

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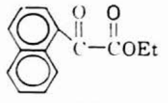
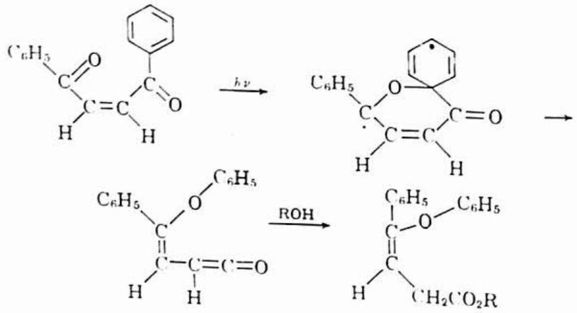
[3] The quantum yield, ϕ, is the ratio of the number of molecules reacting to the number of photons absorbed. It will generally be less than unity, but may be considerably larger if the process under consideration is a photo-initiated chain reaction.



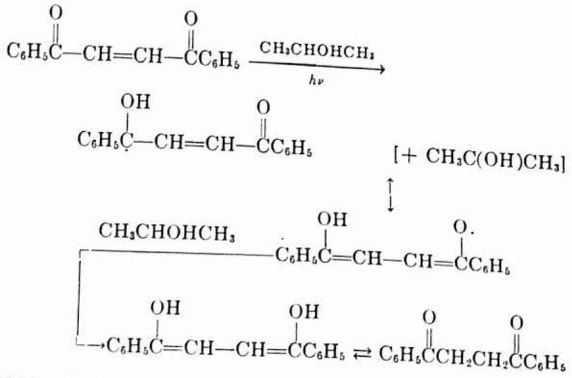
IV

decomposes with a quantum yield of less than 0.01. The investigators present sound spectroscopic evidence that the pyruvate esters decompose from a n-π^* triplet while the naphthoyl ester has a π-π^* lowest triplet. This being the case the excitation is not located specifically in the carbonyl groups but is delocalized throughout the π electron system of the entire molecule. Apparently for this reason the molecule is inert to photodecarbonylation.

An extremely interesting example of the dependence of the *multiplicity* of the excited state on chemical reactivity is found in the recent work of Griffin and O'Connell (*55*). *Cis*-dibenzoylethylene upon direct irradiation in alcoholic solvents (ordinarily good hydrogen donors) is not photoreduced, but rather undergoes extensive rearrangement forming the appropriate ester of 4-phenyl-4-phenoxy-3-butenoic acid. The proposed mechanism involves a 1,5-phenyl migration followed by nucleophilic addition of alcohol to the initially formed ketone.



In the presence of benzophenone the reaction takes an entirely different path with photoreduction *of the double bond* occurring to the exclusion of rearrangement. The chemical mechanism is probably the following:



$$C_6H_5\overset{O}{\overset{\|}{C}}-CH=CH-\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow[h\nu]{CH_3CHOHCH_3} C_6H_5\overset{OH}{\overset{|}{\dot{C}}}-CH=CH-\overset{O}{\overset{\|}{C}}C_6H_5 \quad [+\ CH_3\dot{C}(OH)CH_3]$$

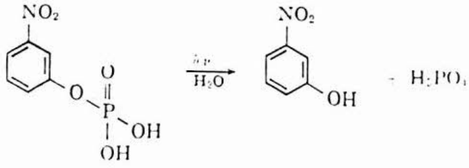
$$\updownarrow$$

$$C_6H_5\overset{OH}{\overset{|}{C}}=CH-CH=\overset{O\cdot}{\overset{|}{C}}C_6H_5 \xrightarrow{CH_3CHOHCH_3} C_6H_5\overset{OH}{\overset{|}{C}}=CH-CH=\overset{OH}{\overset{|}{C}}C_6H_5 \rightleftarrows C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}C_6H_5$$

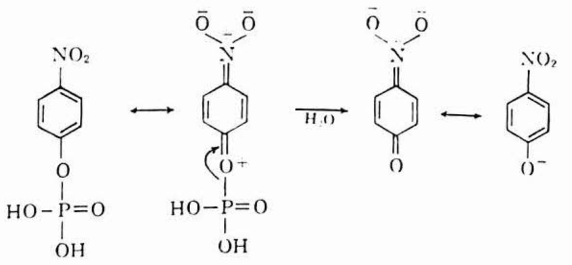
(It is obvious that the alcohol plays a rather different role in the latter reaction, acting in this case as a radical hydrogen donor.) Benzophenone is an excellent triplet excitation donor (sensitizer). In the latter reaction benzophenone excites dibenzoylethylene to its triplet state which subsequently undergoes reduction. Direct irradiation of dibenzoylethylene initially excites the molecule to an upper singlet state which, rather than undergoing intersystem crossing to the triplet, reacts as the singlet. The singlet reaction is the phenyl migration, the triplet reaction is reduction.

Photochemical Solvolysis

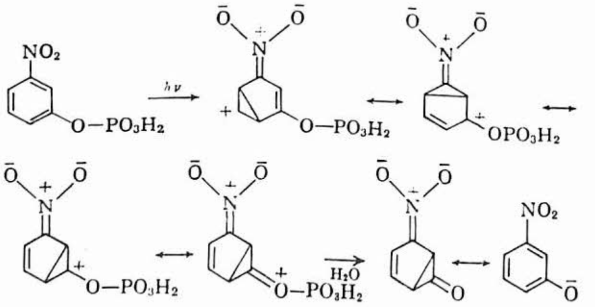
To round out our discussion of photochemical reactivity and the nature of the excited state it seems appropriate to examine a few systems in which the charge distribution in the excited state assists a purely ionic reaction, solvolysis. In 1956 Havinga (*56*) found that in the photochemically induced hydrolyses of meta and para-nitrophenyl phosphate and sulfate esters that the meta compounds were considerably more reactive.



This is, of course, significantly different from what one would expect of the molecules in the ground state, where the electron-withdrawing nitro group selectively activates the ortho and para positions:



Zimmerman and Somesekhara (*57*) have observed the same results with the nitrophenyl phosphate esters and with m-and p-nitrophenyl trityl ether, i.e., unexpected activation by meta-nitro in the light-induced, heterolytic (ion-forming) solvolysis. However, the electronic structure and distribution in the molecule is *not* the same in the ground and excited state. Simple molecular orbital calculations on the lowest π-π^* (singlet or triplet) state show that the greatest withdrawal of electrons by the nitro group is from the meta position, the resonance formulation of which is as follows:



No such assisting structures for the para compound may be drawn. In the case of the nitrophenyl trityl ethers, there was no observable solvolysis of the meta isomer in the dark, where the para compound was solvolyzed easily. *Photochemical* solvolysis of the para isomer showed only a small increase (if any) in rate over the dark reaction, whereas the solvolysis rate of the meta isomer in the presence of ultraviolet light was *ten times* that of the para.

Summary

The aim of this paper has not been to review extensively the field of photochemistry, but rather to present in an elementary fashion examples of the interrelation between photochemistry and electronic spectroscopy. Many of the examples have been taken from the authors' own experience. In attempting to make the material understandable to the nonspecialist, rigor has not been rigidly maintained, especially in the sections on elementary electronic spectroscopy. References (*9–22*), especially those by Kasha, can and should be read by those who wish to pursue the subject further. The general and extensive review of organic photochemistry by Hammond and Turro (*5*) is also highly recommended.

The authors are indebted to Drs. Nicholas J. Turro and M. G. Burford for helpful criticism in the preparation of this manuscript.

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Section 6 Energetics and kinetics

"Energetics and structure of atoms, molecules and ions" may well be called a central theme of modern chemistry. (The word "energetics" seems to scare chemistry students less than the word "thermodynamics".) Certainly the possibility of introducing ideas concerning free energy changes in chemical reactions into school courses is currently receiving much attention from those concerned with curriculum reform. The paper by R. S. Nyholm and H. F. Halliwell discusses the way in which energy can be taught as a unifying concept in science courses. These authors have recently elaborated their views in lectures given to teachers of chemistry in grammar schools and now published in the book *Modern Chemistry and the Sixth Form,* edited by D. J. Millen, London, Collins, 1965. (British sixth form = age group 16-18.)

R. T. Sanderson's paper contains may useful tables of entropies, enthalpies and free energies —reference should also be made to the article on solubility on page 171.

The principles of reaction kinetics are well brought out by J. A. Campbell, using the now well-known "blue bottle" experiment. An expanded version of this paper is now available in book form: J. A. Campbell, *Why Do Chemical Reactions Occur?*, Prentice-Hall Inc., 1964.

Reprinted from *School Science Teaching*, pp. 32-41.

Concepts Basic to a Study of Science

ENERGY AS A UNIFYING CONCEPT IN THE TEACHING OF SCIENCE

Leading paper presented by Professor R. S. Nyholm, F.R.S., University College, London and Mr. H. F. Halliwell, Organiser for Chemistry, The Nuffield Foundation Science Teaching Project

SUMMARY

1 Introduction.

2 The Importance of Energy in Society and in National Development.

3 Energy in the Science Course.

4 The Teaching of Energetics to School Pupils.

1 INTRODUCTION

As teachers of science we frequently complain that some of our colleagues who have been trained mainly or entirely in arts subjects fail to appreciate the need for the allocation of more time for the teaching of our subject. We also complain that these same colleagues, and indeed some educational administrators, do not recognise that science is part of modern culture and that it should occupy a central rôle in the education of all children. However, we in turn, should ask ourselves two questions which seem to bear on this problem: do we teach science in such a manner as to convince pupils and our colleagues that it really is essential for the rounded education of all members of a modern society?; and, do we make the best use of the time which we already have allotted to us? In a moment of self criticism one is tempted to believe that when we can give with confidence affirmative answers to both of the above questions we will be a long way towards obtaining the time—and money—to enable us to teach our subject in the manner that is essential for the preparation of young people for life in the second half of this century.

It is possible to deal here with only one aspect of this problem; we advance the view that unifying concepts which will achieve the objectives below will go a long way towards making our position clear and obtaining the support we need. These objectives are:

(i) Integrating the various branches of science, e.g., chemistry and physics, which divisions are in any case frequently outmoded and artificial. (Thus after separating physics from chemistry and then dividing chemistry into inorganic, organic and physical branches we now solemnly talk about physical chemistry and chemical physics. Furthermore, the chemical physicists often have a chemistry degree and the physical chemists were frequently trained as physicists.)

(ii) Integrating the various branches of a particular subject. As mentioned above the subdivisions of chemistry further encourage a limited horizon in the viewpoint of the student on science as a whole.[1]

(iii) Emphasising the relationship between science and everyday life.

We believe that *Energy* is the most important unifying principle which will achieve the above aims.

It is desirable to set out our views concerning the rôle which we believe science has to play in modern education. Education is a training for a full life in a modern society, carried out in such a manner as to encourage to the maximum the development of the individual personality. Taking the last part of this definition first, it is obvious that science subjects if well taught will do much towards this development of the individual. We all recognise that science is an *experimental* subject and the performance of individual experiments by the pupils encourages expression in a way which can be both exciting and original. Careful observation by the individual is encouraged and scrupulous honesty at all times is emphasised. But when we return to the first part of the definition we need to recognise how truly 'modern' science is. According to Professor D. J. De Solla Price, in his excellent book 'Science since Babylon' between 80 and 90 per cent of all of the scientists who have ever lived are alive today. He points out that 'We might miss Newton and Aristotle, but happily most of the contributors are still with us.' It is a sobering exercise to commence a discussion of this topic by inviting participants to ask themselves how many things which they have used since rising that morning have been developed during the past 50–100 years: radio, electricity, artificial fabrics, transport, etc., spring to one's mind at once. Students must be made to see that the modern world is one largely due to science and no man can claim to be properly educated unless he appreciates *what* science is and *how* it has been responsible for the changed world in which he lives, especially as compared with his 1850 counterpart. Far too often the benefits of science are accepted without any genuine recognition of how these changes have come about. In some countries there is still a real attitude of disdain for science and technology; this view is very ancient, indeed, it is 2,300 years since Plato said, 'Philosophy . . . is the ambition and aspiration of that multitude of pretenders unfit by nature, whose souls are bowed down and mutilated by their vulgar occupations even as their bodies are marred by their arts and crafts.' The ancient Greek 'Democratic State' was a fine place for one to live only if one had chosen one's parents correctly! The same attitude is to be found in 'Gorgias', 'Why is it not the custom for a pilot to give himself grand airs . . . nor for the engineer either . . . who at time saves whole cities . . . ? You . . . despise him and his special art and would call him "engineer" in a taunting sense and would refuse either to bestow your daughter on his son or let your son marry his daughter'. It would be comforting if one could believe that this outlook is no longer held in countries of the West but it is still all too common in many so-called 'educated' circles.

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[1] One is reminded of the fact that this is not new; a famous Professor of medicine was once informed by a very serious medical student that he intended to specialise immediately he finished his degree. On being asked if he proposed to specialise on the Ear, Nose and Throat the student replied that he intended to concentrate on the Nose only. 'Left or Right Nostril?' asked the Professor.

2 THE IMPORTANCE OF ENERGY IN SOCIETY AND IN NATIONAL DEVELOPMENT

Before discussing the way in which energy quantities can be used to understand scientific processes we give some idea of the way in which the use of energy has paralleled social and national development. In his little book 'Man and Energy' Professor Ubbelohde traces the way in which the various sources of power, first animate, and later inanimate have contributed towards the development of our civilisation. The use of human labour was gradually supplemented and eventually overshadowed by power provided by animals such as horses and oxen. The relatively limited use of inanimate water power and wind power changed dramatically during the eighteenth century; since that time man has drawn on fossil fuels such as coal and oil (as well as wood) to motivate his steam engines leading in due course to electrical power and more recently energy released by atomic fission and fusion. To illustrate the increase in energy used per head in the United Kingdom since 1800 this following table is of interest:

Year	Population (millions)	Tons of Coal used per head
1800 . .	8·9	1·1
1830 . .	13·9	2·1
1850 . .	17·9	3·1
1952 . .	49·0	about 5

Thus the energy available per head, ignoring oil fuel, has increased five times in 150 years. In the U.S.A. the increase in undoubtedly greater. Of course not all of this coal is used to produce mechanical power but whether it is used for heating or power it is a measure of energy available.

There is also a close correlation between the standard of living in a country and the per capita consumption of energy. Dr. S. H. Schurr has given some valuable figures in his recent article on Energy in the *Scientific American.* He reduces energy consumption from all sources to its Hard Coal Equivalent. For the year 1960 the figures for a selection of countries are:

Country	Energy consumption per head (Tons) of Hard Coal Equivalent	Country	Energy consumption per head (Tons) of Hard Coal Equivalent
U.S.A.	8·0	Latin American Countries	0·5
Canada	5·6	Middle East Countries .	0·27
United Kingdom . . .	4·9	India	0·14
Common Market Countries .	2·6	Japan	1·2
Australia and New Zealand .	3·0	Communist Asia . .	0·6
U.S.S.R.	2·9		

When teaching in schools it is highly desirable that we correlate the historical development, the current economic position, the current political problems of various countries with their energy problems and relate this with the rate of scientific development.

3 ENERGY IN THE SCIENCE COURSE

Just as it has been shown that the development of a country as a whole is intimately bound up with questions concerning the sources, the amount, and the efficiency of use of energy, so we find that when discussing changes in the structure and properties of matter we are concerned primarily with *energy* changes. The term 'changes in the structure and properties of matter' might well be stressed to students as a means of bringing together chemistry, physics and biology. There is a great need to get away from many of the hackneyed terms of the past. As an example, 'physical and chemical changes' is an expression which can be positively harmful. Students are sometimes asked meaningless examination questions such as 'Is the dissolution of common salt in water a chemical or a physical change?' Although the examiner presumably seeks the reply 'physical', the student is being grossly misled since the process involves hydration phenomena involving the evolution of 200 kilocalories per gram mole of salt, this being used to overcome the large lattice energy of the ionic Na^+Cl^- crystal. This conversion of an Na^+ ion to the $[Na(H_2O)_n]^+$ entity is every bit as chemical as is the formation of 'blue copper sulphate' ($Cu\ SO_4\ 5\ H_2O$) by adding water to the anhydrous salt ($Cu\ SO_4$).)

Unfortunately one of the main problems we face is the fact that teachers all too often lack a sound appreciation of thermodynamics, the subject concerned with the relationship between heat and work. This arises largely from the fact that the subject was in the past frequently taught badly in Universities. There is a need for a simple little book intended specially for teachers summarising the background knowledge of thermodynamics which they should possess. This knowledge is of course much greater than they will need to teach to pupils.

We suggest that the minimum should be as follows:

1 *First Law of Thermodynamics* (Essentially that energy can neither be created nor destroyed). Implicit is the need for an understanding of specific heats at constant pressure and volume and the related gas laws.

2 *Second Law of Thermodynamics* (Essentially that heat will not 'run up hill' spontaneously; work must be done on the system to achieve this). It is very important to appreciate the difference between Free Energy Changes (ΔG), Enthalpy Changes (ΔH) and Entropy Changes (ΔS).

The meaning and use of the simple expressions

$$-\Delta G = RT \ln K_p$$

$$\Delta G = \Delta H - T\Delta S$$

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

are important. An appreciation of Entropy in terms of probability is essential. It is surprising how many teachers do not appreciate the importance of free energy in equilibrium studies. Also many teachers do not fully appreciate why endothermic reactions can occur spontaneously.

3 *The Third Law of Thermodynamics* The determination of entropies from specific heat data should be understood. The way in which phase changes, specific heats, and disorder affect entropies needs to be appreciated.

4 *Important Energy Terms* The importance of terms involved in compound formation and in phase changes need to be stressed. The following are specially important: Heat of Fusion, Heat of Vaporisation, Heat of Atomisation, Heat of Dissociation (of diatomic molecules), Bond Energies (of covalent bonds), Lattice energies (of ionic crystals in particular but also the reason for small lattice energies of molecular crystals), Heat of Ionisation (including Electron Affinity), Heat of Solvation (especially Hydration). The importance of the Born-Haber Cycle for an understanding of the stability of ionic compounds.

We now pass to an examination of just how far we might go with the inclusion of energy concepts in school courses. We refer here primarily to children in the 11–16 age group; for a smaller group in the age range 16–18 the subject will be dealt with in greater detail.

Two questions should, in a simplified form, be constantly in the mind of the teacher and be made evident to the child. When discussing any so-called physical or chemical change the questions should always be raised: 'Can this change occur?' and, 'Will this change occur?'

The piece of paper on which this is printed can burn spontaneously to form carbon dioxide and water and evolve much energy. This is because it is thermodynamically feasible—it has a large $(-\Delta G)$ of reaction. However, it does *not* burn at 25° because of the large energy of activation. Students are well aware of the difference in physics in terms of rolling stones and the use of impedimenta to prevent these moving. A sound appreciation of the meaning of these two questions removes the mystery about catalysis—these merely remove or diminish the importance of the impedimenta restricting the *spontaneous* change which would otherwise occur.

It is suggested that right from the beginning pupils need to be correlating:

(*a*) What they see happening in test tubes, beakers and flasks.

(*b*) The energy changes which accompany these material changes.

(*c*) The molecular or ionic structures of the materials involved in (*a*) and (*b*) and how these enable us to understand (*a*) and (*b*).

Pupils are well aware that apples fall downwards and not upwards but that apples can be made to go upwards if *work* is done on them. Furthermore the falling apple can be made to do the maximum amount of useful work only by allowing the object to fall very slowly and always at equilibrium with the system upon which it is doing work. Every effort should be made to approach gradually the difference between ΔH and ΔG and to emphasise the special importance of ΔG in deciding the position of equilibrium of a reaction. Obviously one needs to choose one's language carefully and not frighten people with thermodynamic terminology. But by choosing suitable examples the difference between the free energy of reaction as a measure of the position of equilibrium and the enthalpy of a reaction can be made clear. Lest we think this is new it is worthwhile reminding oneself that the well-known activity or electromotive series of the metals is simply a list of metals arranged in order of their free energies of reaction with the hydrogen ion. The statement that 'the standard electrode potential of zinc is 0·762 volts' is simply another way of saying that the reaction $Zn + 2\,H^+(aq) \rightarrow Zn^{2+}(aq) + H_2$ can not only proceed spontaneously but if carried out under equilibrium conditions it will make available 35·1 kcals. for useful external work. If however, the zinc dissolves irreversibly in acid 36·4 kcals. of heat are evolved. These two numbers are NOT identical and it is a challenge to us to perform experiments which illustrate this difference and to explain why as soon as possible.

When the age range of the pupils is considered it is clearly seen that there must be a gradual introduction of energetic concepts. It is suggested that these be introduced in four stages:

Stage 1 Develop an awareness of temperature changes. Emphasise whenever a material change occurs that temperature changes, i.e., heat changes occur.

Stage 2 A simple quantitative extension in terms of heat capacity and latent heats for changes in which no new materials are produced. Introduction of energetics in terms of the Kinetic Theory; the relation between average kinetic energy of gas molecules and the absolute temperature. Then pass to a consideration of material changes; a simple picture in terms of bond making and breaking, e.g., for the reaction $H_2 + Cl_2 \rightarrow 2\,H\,Cl$ and in terms of lattice energies for ionic crystals.

Stage 3 Pupils should become generally familiar as soon as possible how we explain the fact that reactions tend to go in the direction in which (*a*) a gas is evolved, (*b*) a precipitate is formed, (*c*) a poorly ionised substance is produced. This will lead to discussions on equilibrium in those cases where there are competing effects, e.g.,

$$Ca\,CO_3 + 2\,H\,Cl \rightarrow Ca\,Cl_2 + H_2O + CO_2^{\nearrow}$$

or

$$Cd\,S + 2\,H\,Cl \rightarrow Cd\,Cl_2 + H_2S^{\nearrow}$$

At this stage the difference between ΔH and ΔG should be made clear.

Stage 4 (more difficult) The significance of the transfer of the thermal energy. A simple explanation of entropy changes in the system and in the environment is now desirable. Reactions in which ΔH is greater than ΔG, roughly equal to it, and less than ΔG should be discussed. The concept of entropy in terms of 'mixed-up-ness' and disorder and as a function of the number of particles involved now arises. This stage will need careful discussion but I believe that it is extremely important that more advanced pupils obtain some idea of the rôle and importance of entropy.

4 THE TEACHING OF ENERGETICS TO SCHOOL PUPILS

The claim has been made that the idea of energy is one of the topics that can and should be an integrating theme for a pupil. It should be integrating not only for a single science subject (and any of the sciences very often seems to be a disintegrated province of study), not only for the group of science subjects commonly met at school (biology, chemistry and physics), but integrating for an understanding of these *and* for those adult activities of engineering, agriculture and national productivity towards which the pupils' generation is moving.

If we want to encourage lively and critical understanding, then integrating, basic, principles are essential. Energetics being one of these, how can we teach it so that we achieve our aim? We shall want to look at this teaching problem of ours very much from the point of view of an individual who is learning as he goes from lesson to lesson: physics, geography, biology, metal or woodwork, games and physical exercises, chemistry, rural science. We must also bear in mind his growth from immaturity to maturity. Although understanding sometimes comes in a flash, it also, and perhaps more frequently, grows slowly from vague beginnings through use and criticism.

We consider the general integrating effect first. To begin with, 'energy' is a vague word linked with warming objects or with moving them. There comes a time for deliberate and explicit consideration of this but only after personal experience of the world. A first, and qualitative step in this direction might be taken at the age of 10 or 11. Previous to that, experience is gradually leading to an awareness that 'I' can warm things or move things, but 'I' get tired, and that the same source that can move things (for example, the sun, a fire or an electricity supply), can also warm things. These kinds of facts the pupil meets in his everyday life and in a great number of school activities, apparently unconnected with 'science lessons'. It is to the latter that we can at first incidentally and later specifically draw his attention. This is the beginning of an effort to make him energy-conscious.

The next stage, perhaps at the age of 11 or 12, will raise and partially answer two questions (*a*) how can this 'energy' be measured? and (*b*) where does this energy come from? There are several ways that lessons could be organised to make it possible for a pupil to look into these points: one would be to embark on an investigation into rain and clouds and evaporating water. Whether this is a part of a 'science lesson' or a 'geography lesson' is only a matter of convenience, but it could involve learning how to use some of the simple tools of investigation so to speak (especially a thermometer), and certainly lends itself to simple graphical representation.

As a result of such work, a pupil could now be more sharply aware of:

(i) the measures of energy for warming—the calorie or the kilo-calorie,

(ii) the heater or the sun as a source of energy,

(iii) the idea of energy being necessary to change water into vapour,

(iv) the idea that moving river water has stored energy from the sun and that this can be harnessed.

During these years, too, a pupil will be investigating two other major topics: the need for, and production of, food (in his biology lessons) and (in the chemistry lessons) what is happening when materials burn. We should see that he is aware not only of the material changes that occur but that energy is needed or energy is produced. In fact, almost any topic that a pupil meets in science, physical exercises, geography, rural studies, can have its energetic aspect brought out if we ourselves are energy conscious. Ploughing the soil needs energy to turn the soil over—whether that energy is supplied by an animal from its food and the air or whether it is supplied by a tractor from fuel and the air. The growing of food-stuffs is seen to be a way in which we make use of the sun's energy. Burning wood (present day vegetable matter) or coal or oil (vegetable matter of ancient times) is a process that enables us to warm or to move things using the energy originally obtained from the sun. We can bring the energetics side out by introducing the pupil to energy levels. At this stage, I do not mean formalised mathematical concepts of physics and chemistry, but just simply putting the bottles of material on the bench and lifting them up onto a laboratory stool on the bench or bringing them down onto the bench. Burning and photosynthesis can have their energetic side very vividly and simply brought out in this way. Representation of this on paper leads easily to the more amenable energy levels we adults are used to.

By the time the pupils are 13, their study of chemistry will have led to an awareness of the different substances the world is made of and to the ideas on molecules and ions and the atoms they are formed from. So too can simple experiments have been done that lead to a link between moving and heating summarised by:

1 Kcal. of energy to raise 3,000 lb. by 1 foot.

A more detailed and formal treatment of work as force × distance may not yet be appropriate. However, it is possible for the idea of energy to become more precise by now and for a pupil to realise that when substances change they give out or take in energy, that this energy can be used for moving and that the extent to which this is done can be measured. Because of their chemistry, these quantities of energy can be expressed as kcal/mole of material change. In fact, the integration we hoped for has begun.

In Biology, we can follow up the fact that

$$C_6H_{12}O_6(c) + 6O_2(g) = 6CO_2(g) + 6H_2O(g) \quad \Delta H = -600 \text{ Kcal.}$$

or that

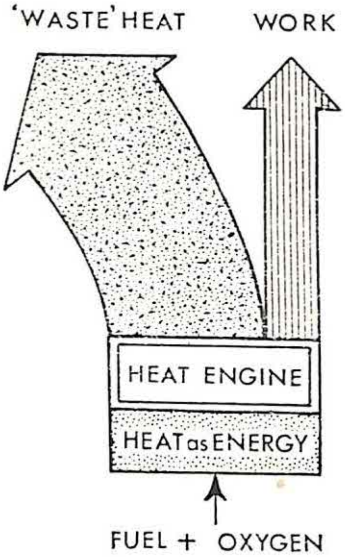
$$6CO_2(g) + 6H_2O(g) = C_6H_{12}O_6(c) + 6O_2(g) \quad \Delta H = +600 \text{ Kcal.}$$

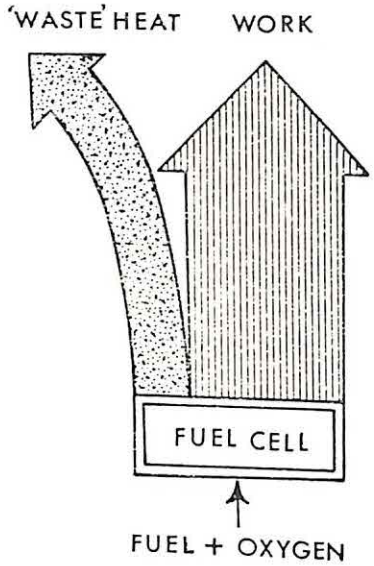
Further questions arise. How does our body act as a machine? What is the energy used for? How much work can we get from the food we eat and the air we breathe? What else is the food used for, and does this process require or supply energy?

In physics we shall perhaps be more concerned with the ways we can invent to harness the energy to do what we want.

In chemistry, we find out more about the materials whose changes are the source of energy.

By the time the pupil is 14 or 15, the idea of energy has become still more precise. Two facts that should become more and more apparent to him are (i) that the energy that can be obtained as thermal energy is seldom the same as that which can be obtained as the energy which will do work for us, (ii) that as we arrange to get more and more work we bring things to a standstill. In fact, the art of power-engineering is to cope with this problem in a profitable way. It is instructive for example to consider the implication of the following pair of diagrams:





An investigation of the way that a simple electrical cell enables us to get 'work' instead of 'heat' from a chemical change can be undertaken with profit and understanding by a 16 year old pupil. Chemistry (as the study of material changes that supply energy) begins to take a fairly prominent position. The ideas and the results of experiments can now be summarised per mole in terms of ΔH (the heat of a reaction), and ΔG (the maximum energy we can use as work).

It is hoped that enough has been said to show how the idea of energy can grow and how it forms a basic and integrating part of all our sciences as well as having valuable repercussions in other types of lessons.

If we turn for a moment to integration within a subject and confine our attention to chemistry, we can see for still older pupils the ideas of energetics can be not only of overall importance but a powerful disciplinary tool for speculation. Quite a number of statements made in less critical textbooks are in fact not acceptable in the light of experimental evidence. Two quotations must suffice:

(*a*) 'Sodium forms monovalent compounds because it loses an electron easily, aluminium on the other hand forms trivalent compounds because it loses three electrons easily'.

Atoms of neither element lose electrons easily—the ionisation energies are known—and in fact it requires slightly more energy to remove three electrons from an isolated aluminium atom than it does to remove TWO electrons from an isolated sodium atom.

(*b*) 'The electrochemical series is seen to be controlled by the ease with which the metals lose electrons'.

In fact (ionisation energies and hydration energies are known) the energy required to convert an isolated zinc atom into a zinc ion in water is very nearly the same as that required to convert an isolated copper atom into a copper ion in water. The reactivity of zinc compared with copper is more reasonably associated with the difference in the metallic bonding in the two metals. This is not necessarily true for other metals: a study of the energies involved should be undertaken before we broadcast rash statements.

In chemistry, we shall want to build up towards a realisation of the importance of the energy available to do work (ΔG) and the relationship between it and the equilibrium conditions and the overall energy change in the system (ΔH) viz,

$$-RT\ln K = \Delta G = \Delta H + \text{(the limiting thermal energy that the environment demands).}$$

The latter term which accounts for the difference between the 'heat' and the 'work' of a reaction, can be understood in terms of the number of ways systems can hold their energy. Two factors, therefore, influence the likelihood of a change taking place, but consideration of this and the way it can be taught must wait for later discussion groups.

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Principles of Chemical Reaction

Among the fundamental questions of chemistry, none seems more important than this: Why do chemical reactions occur? The purpose of this paper is to examine the nature of chemical change, in the hope of recognizing and setting forth the basic principles that can help us to understand why. For the very essence of practical chemistry is the scientific control of chemical change. If we know why it occurs, then we can know what conditions are necessary to cause or prevent its occurrence, and we can direct our ingenuity toward establishing such conditions. Furthermore, such understanding should be invaluable to students, who without it are faced with an almost infinite variety of chemical equations to be memorized but with no basis for recognizing that they do make sense.

Nature of the Problem

Before we can consider *why* reactions occur, it is necessary to think of *what* happens in a chemical reaction. Briefly, reactants change to products. In order for this to happen, atoms which are initially attached to one another in a certain way in the reactants become separated, at least to some extent, and rearranged in the products. Since the initial attachment can only exist if the forces of interaction among the component atoms are predominantly attractive, energy must be expended to produce the chemical change. But this is not all that is required. The atoms in the reactants must be so arranged that some reasonable mechanical pathway exists to permit the formation of products, or else the reaction cannot occur. Furthermore, even if energy and a mechanical pathway are available, there may be little tendency for the reaction to proceed. Two aspects of this need consideration, and both may be approached from the viewpoint of separated atoms. If we imagine all the atoms that might be involved in a given reaction to be initially separated as a atomic gas, then we can consider whether they are more likely to form the substances labeled "reactants" or those labeled "products," and which are more stable. From the atomized state to the combined states, the change is from highly random to much more orderly arrangement of atoms, and we may reasonably expect the change which involves least departure from the original randomness to be more probable. But we may also reasonably expect that the formation of the strongest bonds, and therefore the most stable aggregates, will also tend to be favored.

Our problem, then, is to consider these several aspects of chemical reaction and to try to recognize those fundamental principles that may lead to a comprehensive, unified interpretation of chemical change.

Kinetics and Reaction Mechanism

Unquestionably we would find it most helpful toward understanding what reactions are possible if we could observe directly the activities of the individual atoms and molecules to see what they can and cannot do. Forever lacking the ability to make such observations, we can still infer what they must be from experimental measurements of reaction rates of the subtances in bulk. The study of kinetics then can lead to valuable information concerning the mechanisms by which reactions probably occur and the activation energies required. But such information is chiefly descriptive; and although, for example, a knowledge of the activation energy needed can help explain why a given reaction may proceed rapidly or only very slowly under specified conditions, the basic question as to why the arrangement of atoms in the products should be favored over that in the reactants remains unanswered.

The Nature of Spontaneous Reaction

Our chief concern here is therefore with the nature of the initial and final states and not with the rates or mechanisms of the various transition processes. For ultimately it is only the qualities of these states that determine which is more likely to result from a spontaneous reaction of the other.

The meaning of "spontaneous" needs to be clearly understood. It is commonly used to describe reactions which begin at once as soon as contact between reactants is made. For example, a substance is "spontaneously inflammable" if it bursts into flame when exposed to oxygen, without the help of any external agent. But although such examples are spectacularly obvious examples of spontaneity, they constitute only a small proportion of what are more generally called "spontaneous" reactions. The real meaning of "spontaneous" is "having the potential to proceed without the assistance of external agency." It implies nothing about mechanism or rate; and when a reaction is called spontaneous this is no indication as to how or whether it will proceed under the given conditions. Nevertheless, the *direction* of spontaneity remains the most important property of a chemical reaction.

As mentioned earlier, two factors determine the relative tendency of separated atoms to come together in a given way. One is the strength of the bonds formed. The other is the probability or degree of randomness in the final state. A reaction tends to occur spontaneously in the direction of stronger bonds and less organized array. These two influences on the spontaneity of chemical change are jointly taken into account by the thermodynamic function called the "Gibbs energy," designated as G.[2] This function, the "net energy" or "useful energy" at constant pressure, is defined as the difference between the total energy content or enthalpy, H, and the energy that is unavailable for useful work, which is a product of the probability, or randomness, or degree of disorder, called entropy, S, and the absolute temperature, T:

$$G = H - TS$$

The entropy is evaluated as the energy change per degree, "entropy units" being calories per degree per mole. Multiplication by the absolute temperature gives the energy associated with the probability at that temperature, or the energy unavailable for useful work. For a chemical reaction, *changes* in free energy, heat content, and entropy are the quantities of interest:

$$\Delta G = \Delta H - T\Delta S$$

The first and foremost fundamental principle of chemical reaction is therefore the following:

(1) Chemical reactions tend to proceed spontaneously in the direction of diminished free energy content, which means when the free energy change, ΔG, for the reaction is negative, free energy is released.

According to the above expression, chemical reaction tends to proceed spontaneously at constant pressure only under one of the following sets of conditions:

If the total bonding forces in the products exceed those in the reactants *and* the total disorder (entropy) of the products is higher;

If the total bonding forces in the products exceed those in the reactants and the total disorder in the products is lower but not enough lower to make $T\Delta S$ greater than ΔH; or

If the total bonding forces in the products are weaker than those in the reactants but the entropy increase (increase in disorder) is more than large enough to compensate for the heat absorbed.

Where these two influences of bond strength and entropy are in conflict, the final outcome will depend on their relative contributions in the reaction. The factors determining the magnitude of these relative contributions may now be considered in some detail.

Principles of Entropy

(2) The gaseous state is more probable than the liquid state, which in turn is more probable than the solid state.

In other words, the atoms or molecules of a gas are more independent of one another than in a liquid or solid, and therefore can become more randomly distributed, which corresponds to higher entropy. Melting involves an increase in entropy, and vaporization a still further increase in entropy. Since in the liquid state the motion of the molecules is still highly restricted, the entropy of melting is relatively small. The difference in orderliness between liquid and gas is very much greater, corresponding to an entropy of vaporization which is relatively large. For "normal" liquids, those in which the chief intermolecular attractions are van der Waals forces, the entropy of vaporization is nearly independent of the composition, about 22 entropy units. This entropy is larger if stronger polar interactions or protonic bridging occurs in the liquid, because a greater effort toward disorder is then required for the vaporization process. For many of the chemical elements, the entropy of melting is also nearly constant, having the value of 2.3 entropy units. Some values of the entropy at 25° of various substances in gaseous, liquid, and solid states are given in Table 1.

Table 1. Entropy of Various Substances at 25° (eu) (2)

Substance	Solid	Liquid	Gas
Na	12.30	13.83	36.71
P	9.82	10.28	38.98
Si	4.43	11.21	40.12
Pb	15.5	17.14	41.89
H_2O	...	16.72	45.11
CH_3OH	...	30.3	56.8
B_2O_3	12.91	18.55	64.42
SiO_2	10.00	11.35	54.62
Li_2O	8.98	9.86	56.03
BeO	3.38	10.50	47.21
TiO_2	12.01	15.43	56.44
PbO	15.59	20.55	57.35
BCl_3	45.3	...	85.3
$SiCl_4$	....	57.2	79.2
$PbCl_2$	32.50	38.34	76.63
NaCl	17.33	20.22	54.88
$HgBr_2$	40.71	46.80	76.51

According to this principle, the presence of a gas among the products but not the reactants suggests that the entropy of the products probably is greater than that of the reactants. This tendency exists because the entropy differences among different solids and or liquids tend to be lower than the differences between the gaseous state and the solid or liquid state. Entropy changes thus tend to favor decomposition or interaction of solids or liquids to form gaseous products.

(3) A monatomic gas is more probable than a polyatomic molecular gas, and hence tends to have higher entropy.

Greater disorder is the condition of the monatomic gas. Formation of polyatomic molecules, with their fixed and definite structure, increases the order and therefore decreases the entropy. Some examples are given in Table 2. In a gaseous reaction, then, the entropy change favors dissociation of larger into smaller molecules, or any metathesis (double decomposition) that increases the total number of moles of gas.

Table 2. Entropy of Monatomic and Polyatomic Gases (eu/g atom) (2)

H	27.4	H_2	15.6		
N	36.6	N_2	22.9		
O	38.5	O_2	24.5	O_3	19.0
F	37.9	F_2	24.4		
Si	40.1	Si_2	17.5		
P	39.0	P_2	26.1	P_4	16.7
S	40.1	S_2	27.3	S_8	12.9
Cl	39.5	Cl_2	26.6		
NO_2	57.5	N_2O_4	36.4		

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[2] This is the quantity usually referred to by Lewis and Randall-trained chemists as "Free energy" or "Gibbs free energy" designated by F. The terminology here used follows the IUPAC recommendations.

(4) **An amorphous solid is more probable than a crystalline solid, and a simple crystalline solid more probable than a more complex crystalline solid.**

The formation of simpler substances from more complex ones is therefore favored by the entropy change.

(5) **A molecular addition compound, or a coordination complex, is less probable than its separate components.**

The formation of such compounds is therefore accompanied by a decrease in entropy, which consequently increases the requirement of bond strength needed to hold together a stable aggregate.

(6) **Compounds of elements of higher atomic weight, or molecules of the free elements themselves, tend to have higher entropy.**

A number of examples are given in Table 3. The explanation presumably lies in the effects of mass on the intra-crystalline or intra-molecular vibrations. The greater the mass, the lower the vibration frequency and thus the more probable the state, and the higher the entropy. This effect seems to predominate over minor effects originating in differences among crystalline forms as shown in Table 4.

Table 3. Effect of Mass on Entropy of Gases at 25°C (eu) (2)

X =	F	Cl	Br	I
HX	41.51	44.65	...	...
NaX	51.70	54.88	...	...
MgX_2	55.89	61.50	...	...
PbX_2	69.35	76.63	82.43	85.91
BX_3	60.71	69.32	...	...
ZrX_4	76.95	87.37	98.78	108.42
NOX	59.27	...	65.38	67.67

Table 4. Effect of Mass on Entropy of Crystalline Solids (eu) (2)

LiF	8.57	PbO	16.2	CaF_2	16.46
NaF	14.0	PbS	21.8	$CaCl_2$	27.2
KF	15.91			$CaBr_2$	31
		Li_2CO_3	21.60	CaI_2	34
Na_2O	17.4	Na_2CO_3	32.5		
Na_2S	23.4			$MgCO_3$	15.7
		$ZnSO_4$	29.8	$CaCO_3$	22.2
BeO	3.4	$CdSO_4$	32.8	$SrCO_3$	23.2
MgO	6.4			$BaCO_3$	26.8
		MgH_2	7.5		
MgO	6.4	MgF_2	13.7	$MgSO_4$	21.9
MgS	11.0	$MgCl_2$	21.5	$CaSO_4$	25.5
				$SrSO_4$	29.1
				$BaSO_4$	31.6

(7) **At ordinary temperatures, entropy effects are commonly small enough to have relatively little effect on the direction of reaction unless the difference in total bonding energy between reactants and products is relatively small.**

This is well illustrated in Table 5 by comparison of ΔH and ΔG values for the formation of a number of chemical compounds in their standard states, and for a number of chemical reactions in Table 6. It was this fact that led Berthelot and Thomsen to believe that the heat of a reaction was the sole factor determining the direction of spontaneous reaction, but this was before the concept of entropy had been clearly recognized. Entropy units are *calories* per degree per mole, and the entropy changes accompanying reaction are often only a few entropy units, whereas heats of reaction are commonly more than a *kilocalorie* per mole. Thus even though the entropy is multiplied by about 300°K (at ordinary temperatures), the product does not even equal one kilocalorie unless the entropy is more than 3. If the ΔH value for a reaction is relatively large, say -10 kcal per mole or greater, one can reasonably be confident in predicting spontaneous reaction in that direction.

Table 5. Comparison of Enthalpies and Free Energies of Formation (kcal mole^{-1}) (2)

	$\Delta H_f°$	$\Delta G_f°$
H_2O (1)	-57.80	-54.64
HCl (g)	-22.06	-22.77
SO_2 (g)	-70.96	-71.79
H_2S (g)	-4.82	-7.89
H_2Te (g)	36.9	33.1
KNO_3 (c)	-117.76	-93.96
Na_2CO_3 (c)	-270.3	-250.4
$Al_2(SO_4)_3$ (c)	-820.98	-738.99
NH_3 (g)	-11.04	-3.98
N_2O_4 (g)	2.31	23.49
HNO_3 (1)	-41.40	-19.1
PH_3 (g)	2.21	4 36

Table 6. Comparison of Standard Enthalpies and Free Energies for Some Chemical Reactions

	$\Delta H°$ (kcal)	$\Delta G°$ (kcal)
$CCl_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl\,(g)$	-41.2	-61.2
$SF_6(g) + 3H_2O(g) \rightarrow SO_3(g) + 6HF(g)$	-45.0	-75.9
$CaO(c) + CO_2(g) \rightarrow CaCO_3(c)$	-42.5	-31.1
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$	-191.8	-191.4
$AsCl_3(l) + 3NaF(c) \rightarrow 3NaCl(c) + AsF_3(g)$	-24.7	-31.7
$AlBr_3(c) + PCl_3(g) \rightarrow AlCl_3(c) + PBr_3(g)$	-3.1	-4.3
$CH_3OH(l) + NH_3(g) \rightarrow CH_3NH_2(g) + H_2O(g)$	3.5	-4.3

(8) **All chemical reactions that increase the entropy occur spontaneously at high enough temperatures.**

Although the heat of reaction changes only relatively slowly with temperature, the entropy effect is the product of the entropy and the temperature. No matter what the heat of reaction, therefore, if the entropy change is positive and multiplied by a large enough temperature, the product $T\Delta S$ will be subtracted from the heat of reaction to give a negative free energy change. This is a very important principle, accounting for the existence at high temperatures of species unknown at lower temperatures because of their tendency to form more complex aggregates stable at the lower temperatures. As already observed, decompositions of compounds increase the entropy, and thus tend to proceed spontaneously at high enough temperatures.

The special significance of this principle is that although enthalpy changes tend to dictate the course of reaction at ordinary temperatures, *the relative importance of entropy increases at higher temperatures until it becomes the dominant factor.*

Principles of Bond Strength

At the outset, a distinction should be made between "stability" and "reactivity." Unfortunately, it is common practice to confuse the two. Too frequently a substance which is relatively reactive is called "unstable" although actually its bonds may be very strong. In view of this ambiguity, it would seem much more preferable to use the word "stable" only to describe the condition of being held together by strong bonds and to imply the requirement of high temperature to disrupt the substance without regard to its possible chemical reactivity. An "unstable" substance may then be unreactive or highly reactive, but it must be one held together by weak bonds that are thermally disrupted at relatively low temperatures.

In an earlier paper (*3*), principles of chemical bonding were set forth to summarize the requirements of bond formation. Here it is desirable to examine the factors that may influence bond strength. This is unfortunately a very complex subject, to be dealt with at present only in a qualitative or at best a semiquantitative way. But still it is possible to state some useful generalizations. In fact, for at least some kinds of compounds, notably the binary halides, it has been found possible recently (*4*) to calculate quantitatively the total bonding energy, from application of the following principle:

(9) In the binary halides, and possibly other classes of compounds as well, the total bonding energy (per equivalent) varies directly with the partial charge on halogen and the bond order and inversely with the bond length.

This principle holds regardless of the nature of the bonding, as shown, for example, by the fact that all the binary chlorides of the major group elements fall on the same straight line connecting Cl_2 with NaCl, formed by plotting partial charge on chlorine against the function RH/n (where n is the bond order, H the heat of atomization per equivalent, and R the bond length). Some representative examples of the agreement between calculated and observed bond energies are given in Table 7. Much remains to be done in the development of a bonding theory to account for these remarkable relationships; but by bringing together "ionic" and "covalent" bonding within a unified system, it promises eventually to permit the more complete understanding needed for predicting more precisely the direction of spontaneous change.

Table 7. Total Bonding Energy and Polarity of Some Representative Examples

	$-\delta x$	H(calc)[a]	H(exp)[a]
LiF	0.74	206	202
LiI	0.53	127	129
NaF	0.75	181	181
NaI	0.54	120	120
$BeCl_2$	0.23	129	128
MgI_2	0.19	88	86
$BaCl_2$	0.49	154	152
AlI_3	0.12	72	76
CF_4	0.09	99	103

[a] Heat of atomization per equivalent.

Reverting now to the more conventional views of bonding, we may observe certain principles that can be helpful meanwhile.

Normal Covalence

(10) Covalent bonds between small atoms tend to be stronger than covalent bonds between larger atoms.

Some examples illustrating this principle are listed in Table 8. The importance of coulombic forces in covalence suggests that since such forces vary inversely with the square of the distance of separation of the charges, greater strength of bonding between smaller atoms is probably the result of closer interactions of opposite charges. Larger atoms not only form longer bonds, but also have a larger number of nonbonding electrons that may tend to weaken the bonding through inter-cloud repulsions. This effect appears to outweigh the effect of attraction resulting from the increased nuclear charge.

Table 8. Relation of Bond Strength to Radius (or Bond Length)

	r (Å)	E (kcal)
H_2	0.37	104
C—C	0.77	83
Cl_2	0.99	58
S_8	1.02	54
Br_2	1.14	45.5
I_2	1.33	35.6

(11) Covalent bonds between atoms tend to be weaker, the greater the difference in principal quantum number of the valence shell of the two elements.

Evidently, as exemplified by the illustrations of Table 9, the overlapping, or coalescence, of orbitals becomes less effective when the atoms are very unequal in size. This is particularly well illustrated by the binary hydrogen compounds having covalent bonds of relatively low polarity (*5*).

Table 9. Relation of Bond Strength to Difference in Valence Level

Compound	Difference in n	Decomposition (°C)	Av. bond energy (kcal)
CH_4	1	800	99.4
PH_3	2	300	78.0
GeH_4	3	285	...
TeH_2	4	25	56.9
SbH_3	4	25	...

(12) Covalent bond strength tends to be greater, the greater the bond polarity.

One explanation of this tendency has been provided by Pauling (*6*), who considered the extra energy resulting from bond polarity to be derived from supplementing the covalent bond energy with the ionic attraction between unlike charges. He used this extra energy in establishing his well-known scale of electronegativity. In general, a closer interaction between bonding electrons and nuclei appears possible in polar bonds because they are shorter. This shortening can be explained (*7*) by considering that uneven sharing of the electrons produces a radial contraction of the partially positive atom that is greater than the radial expansion caused by the acquisition of partial negative charge by the other atom. A rough quantitative indication of the effect of different polarity in bonds between the same two atoms is provided by the heats of atomization (per equivalent) of binary compounds exhibiting different oxidation states. Some examples are given in Table 10. Invariably, the heat of atomization is lower the higher the positive oxidation state of the central atom. This is because the more competitors there are for the electrons of a given atom, the less successful each will be in acquiring negative charge, and correspondingly the less polar its bond.

Table 10. Heats of Atomization of Some Binary Compounds (kcal/equiv) (2)

CrF_2	157.0	$TiCl_2$	141.9	$TiBr_2$	131.0
CrF_3	139.1	$TiCl_3$	121.1	$TiBr_3$	108.2
MnF_2	147.4	$TiCl_4$	101.6	$TiBr_4$	93.9
MnF_3	128.2	AuCl	121.7	CuBr	132.9
PbF_2	121.7	$AuCl_3$	63.9	$CuBr_2$	83.9
PbF_4	86.3	$SnCl_2$	106.4	$SnBr_2$	94.5
ClF	60.9	$SnCl_4$	79.2	$SnBr_4$	69.0
ClF_3	40.9	PCl_3	82.2	PBr_3	69.1
BrF	64.1	PCl_5	66.7	PBr_5	55.9
BrF_3	52.9	$SbCl_3$	79.9	FeO	111.4
SO_2	61.6	$SbCl_5$	62.1	Fe_2O_3	95.0
SO_3	55.0				

Bonds between hydrogen and highly electronegative elements such as fluorine, oxygen, and chlorine are especially strong, the relatively positive hydrogen atom having no underlying electron shells to restrict the closeness of interaction with the other atom. The significance of this extra strength in influencing the course of reaction will be mentioned later.

(13) **Covalent bonds between atoms each bearing partial positive charge tend to be less stable.**

Instead of being shorter than normal, as might be predicted from the fact that positive charge should correspond to contracted electronic spheres, such bonds tend to be as long or longer than expected from their nonpolar covalent radii. This corresponds generally to a bond weakening, that may be the result of reduced availability of outer electrons for sharing.

Table 11. Some Unstable Molecules Having Bonds between Positively Charged Atoms

	Charge on	Element
Si_2H_6	0.18	Si
N_2O_4	0.11	N
P_2Cl_4	0.26	P
B_2Cl_4	0.36	B
TNT	0.10	C

Some examples of molecules whose instability may at least in part be ascribed to such causes are listed, with the positive charge on adjacent atoms, in Table 11. (Notable exceptions are the fluorocarbons, whose C—C bonds appear to be unweakened by the relatively high partial positive charge on the carbons. Perhaps the weakening does exist, but is compensated for by coulombic attractions between positive carbon and the negative fluorines attached to its immediate neighbors.)

(14) **Covalent bonds having partial multiplicity as a result of resonance are more stable than single bonds or than the equivalent of partial multiplicity in separate single and integral multiple bonds.**

The validity of this principle appears to be established by the existence of resonance—by the equalization of bonds toward partial multiplicity, wherever possible, instead of by separate single and double bonds. The explanation may perhaps be found in the apparent increase in interelectronic repulsions that occur when an atom acquires electrons. This increase seems to mean that the shared electrons contribute most to the stability as they are first acquired partially. Greater stability therefore results when two atoms (or sometimes more) each hold the bonding electrons partially than when each simply holds its own completely. This is why covalent bonds form, and why their rupture always costs energy. Similarly, then, if a double bond might be in one of two places in a molecule but cannot be in both places at once, it tends to become distributed partially in both locations, rather than totally in one to the exclusion of the other. This kind of situation is called *resonance;* it occurs wherever it is possible because it produces greater stability. In fact, wherever formation of single covalent bonds would leave at least one otherwise vacant orbital on one atom and one or more pairs of otherwise unshared outer electrons on adjacent atoms, we may expect further interaction in which at least partial use of these orbitals and electron pairs is made to strengthen the bonding through multiplicity.

Some of the most significant examples of bonds where partial multiplicity is to be expected occur in compounds of fluorine and oxygen with elements whose atoms have outer vacant orbitals available. Fluorine, being highest of all elements in electronegativity and having but one valence orbital vacancy, is generally considered capable of forming only a single covalent bond. Several facts suggest, however, that such a bond can be partly multiple under appropriate conditions. The fluoride ion is known to act as donor in many complexes; partially negative fluorine may act likewise, although probably to a lesser degree. The weakness of the bond in F_2 has been explained as resulting from interference of nonbonding outer electron pairs on the two atoms, suggesting that such pairs are in a position to interact attractively with another atom if it has vacant orbitals available. Furthermore, bonds of other elements to fluorine are frequently disproportionately strong and unexpectedly short, both of which suggest partial multiplicity. The bond lengths in fluorides of other highly electronegative elements are as would be predicted from adding the covalent radii; but to less electronegative elements the calculated radius sum commonly must be divided by 0.94 to give the observed bond length, indicating a bond order approximating 1.5.

Further evidence in support of the partial multiplicity in fluorine bonding is available from its resemblance to oxygen, which, forming two bonds, discloses something of the nature of its bonding by the bond angle. Although two single bonds to oxygen would be expected to make an angle not exceeding 109° (Cl_2O, 110.8°; F_2O, 103.2°; H_2O, 104.5°), many examples are known where the angle is much larger, even approaching 180°. For example, in numerous silicates and the silicones, the Si—O—Si angle is in the range 140–150°; in P_4O_6 the P—O—P angle is 128°, as it is also in As—O—As and Sb—O—Sb; and in various borates the B—O—B angle may be in the range of 120–140°. All such wider-than-expected angles suggest partial utilization of the two otherwise unused pairs of outer electrons on the oxygen, involving the fourth sp^3 orbital of boron or outer d orbitals of the silicon, phosphorus, and others. If oxygen can enter into such partial multiplicity, there seems to be no reason why fluorine cannot do so similarly.

As a probable consequence of such partial multiplicity, heats of atomization (per equivalent) of BF_3 (154.5), B_2O_3 (126.9), AlF_3 (148.5), Al_2O_3 (121.9), SiF_4 (137.8), SiO_2 (107.2), AsF_3 (114.9), and similar compounds are appreciably higher than would be expected from polarity. When the average bond energies for all the gaseous molecules listed in NBS Circular 500 (*2*) are arranged in descending order, the leaders are: B—F, Si—F, H—F, Li—Cl, Na—F, As—F, H—O. As will be seen, these facts become especially important when one attempts to predict the course of reactions involving such compounds.

Coordination

This topic could easily lead us into more elaborate and lengthy discussions than would be appropriate to our primary purpose of establishing practical rules for understanding chemical reactivity. Such discussions would pertain to the chemistry of transition metal complex ions, and would involve exposition of ligand field theory more specialized and detailed than was intended for this paper. This is an interesting and active area of research but cannot be included here. Instead, let us consider some of the more general aspects of coordination bond formation, as it occurs in both molecular addition compounds and complex ions in general.

(15) **Coordination bonds tend to be stronger, the more readily the donor atom can supply electrons.**

Factors influencing the ability of a donor atom to furnish a pair of electrons to an acceptor may include the following:

(*a*) *Its Partial Charge.* An electron pair is not readily donated by an atom from which other electrons have been partially withdrawn. For example, neither nitrogen trifluoride nor $(CF_3)_3N$, in which the nitrogen atoms bear partial positive charge, are effective donors. Even when other electrons have not been withdrawn from the donor atom, but the donor atom is of a highly electronegative element and only bears small partial negative charge in the compound, it is not an effective donor. For example, the oxygen in the nitrate ion or the sulfate ion is not highly negative and does not donate electrons very easily (see also under (*e*)). On the other hand, if the donor atom is highly negative, even though it may initially have been high in electronegativity, it can function well as donor. Oxygen in state of relatively high negative charge is effective as a donor; for example, hydroxide ion (charge on oxygen −0.67) is a better donor than water (charge on oxygen −0.25).

When two or more elements are joined together in a negative ion, and atoms of each contain unshared electrons in the outer shell, these electrons are expected to be donated more readily, the less electronegative the original element. For example, in a cyanide ion, both carbon and nitrogen bear unshared electron pairs but the carbon is probably the more ready donor. In anions containing both nitrogen and oxygen as potential donors, it is probably the nitrogen that donates more readily. When the original element is only intermediate in electronegativity, such as phosphorus, then it can act as donor in compounds where it even has a small partial positive charge, as in $P(CH_3)_3$, especially provided the attached atoms or groups are good electron suppliers (see (*c*) below).

Closely related to this donor ability is the observation that the higher the negative charge on a donor, the greater its coordination number in a crystal lattice (*4*).

(*b*) *Involvement of the Donor in Bond Multiplicity.* An electron pair is less available for coordinate bond formation when it would otherwise be involved in multiple bonding through resonance. For example, the partial charge on nitrogen in trisilylamine, $(SiH_3)_3N$, should be more negative than that in trimethylamine, since silicon is less electronegative than carbon. Therefore trisilylamine should be a better donor, but in fact it is scarcely effective. The reason is believed to be that the outer d orbitals of the silicon are able to involve the "unshared" pair of electrons on the nitrogen to such an extent that they are effectively utilized in nitrogen-silicon "pi" bonding and thus unavailable for donor action, toward an outside acceptor.

(*c*) *Capacity of the Reservoir Attached to the Donor.* Donor atoms appear to be better able to supply electrons, the better the electron reservoir that is made available to them by other atoms covalently bonded to them. For example, $P(CH_3)_3$ is a better donor than PH_3; this may be ascribed to the fact that the methyl groups supply electrons to the phosphorus more effectively than the hydrogen atoms can, thus permitting phosphorus atom to share its extra pair of electrons more easily with an outside acceptor.

(*d*) *Polarizability of the Donor.* The donor may be more effective in some combinations if it is relatively easily polarized, as for example, the iodide ion compared to the fluoride ion.

(*e*) *Concentration of the Donor Electron Pair.* Donor atoms may be able to function better, especially toward small atom acceptors, when their electron pairs are concentrated within a relatively narrow region rather than spread out. For example, alcohols and ethers are generally better donors than ketones or carboxylates, for the probable reason that in the former the oxygen is already involved in two single bonds, whereas in the latter, it is involved in one double bond. Although in both cases the oxygen has two "free pairs" of electrons, these electrons have more room to spread out when the other electrons are localized in the double bond rather than distributed in two single bonds.

This is especially important in protonic bridging or indeed in any bonding to hydrogen. For a covalent bond to hydrogen may sometimes usefully be considered a coordination bond in which a proton is attached to a donor, and a protonic bridge is similar in that a partially positive hydrogen (instead of a bare proton) is attracted to a donor. In the first case, the acidity of the hydrogen, and in the second, the strength of the protonic bridge, are largely determined by the availability of the electron pair in a concentrated form. In the first case the hydrogen is more acidic the less available the electron pair, since a poor donor to the proton permits more extensive dissociation in a solvent that is a competitive donor. For example, HCl is more acidic than HF probably because the electron pairs on the larger chloride ion are too spread out to serve as effectively as the more concentrated electron pairs on the smaller fluoride ion. For essentially the same reason, then, molecular HF is strongly associated through protonic bridging whereas HCl is not.

Examples involving oxygen are water, and nitrate ion. The charge on oxygen is -0.25 in the former and -0.29 in the latter. Water is nevertheless a much more effective donor than is the nitrate ion. The difference may well lie in the multiple nature of the bonding in the latter, giving the "donor" pairs that are unused in bonding to nitrogen more opportunity to spread out, thus making them less available to an outside acceptor.

(16) **Coordination bonds tend to be stronger, the more effective the acceptor.**

Factors influencing the ability of an acceptor atom to take on electrons may include the following:

Partial Charge. Other factors being equal, one would expect an acceptor to attract an electron pair more strongly, the higher its partial positive charge.

Available Orbitals. Acceptor atoms may be able to form more stable coordination bonds when they have more than one vacant orbital available to be used in bonding to the same donor, as in transition metal atoms having several available *d* orbitals.

Involvement of the Vacant Orbital in Partial Multiple Bonding. Acceptor atoms are less effective when the "vacant" orbital can be at least partly used in multiple bond resonance within the molecule. For example, $BI_3 > BBr_3 > BCl_3 > BF_3$ despite the increasing positive charge on the acceptor atom, presumably because this is the order of increasing multiplicity using the acceptor orbital.

Ionic Bonding

(17) **The strongest ionic bonding is expected between the smallest ions of highest charge, and vice versa.**

The question of whether ions actually exist as such in the lattice of crystals formed by combination of such "ions" has been discussed previously (*3, 4*) and will not be considered again here. This statement is simply based on Coulomb's law, assuming the "ions" to be particles with their net charge centered at their nuclei. The effect of ion size is illustrated by comparison of the physical properties of LiF, which melts at 845° and boils at 1681°, and CsI, which melts at 621° and boils at 1280°. The heats of atomization are 203 and 125 kcal/mole.

(18) **When size difference between cation and anion is great enough to permit anion-anion or cation-cation contact, the ionic bonding is weakened by these repulsions.**

For example, lithium iodide contains cations so small in comparison to the anions that the anions must be in direct contact, reducing the lattice energy as shown by otherwise unexpectedly low melting and boiling points (*6*).

(19) **Ionic crystals containing complex anions tend to decompose more readily, the less completely the anion has acquired the electrons of the cation and the smaller and therefore more polarizing the cation** (8).

Calcium carbonate is less stable than barium carbonate but more stable than zinc carbonate; magnesium sulfate is less stable than calcium sulfate; and sodium borohydride is less stable than potassium borohydride.

Steric Requirements in General

No matter what kind of bonding may be in effect, it must be weakened if the most stable bond angles or the most stable distances are not allowed because of interference in space of two or more groups in the same molecule or because of any distortion that might be necessary to complete the bonding in the molecule.

For example, carbon tetraiodide is not very stable presumably because the four iodine atoms tend to get in one another's way. P_4 and cyclopropane are not very stable because their formation requires the distortion of normal bond angles, with consequent crowding together of electrons of the separate bonds.

Metallic Bonding

(20) **The strength of metallic bonding tends to be greater, the greater the number of half-filled orbitals possible, including the underlying *d* orbitals.**

Nearly all of the transition metals seem to have stronger bonding than the nontransition metals, showing the greater utility of *d* orbitals for this purpose. In both types of metals, as roughly indicated by the heats of atomization, bond strength is lowest where there are fewest valence electrons or fewest orbital vacancies and works toward a maximum where all bonding orbitals are half-filled. This is illustrated by Table 12. Evidently the more bonding electrons, the stronger the bonding, provided vacancies are available. This is consistent with the facts of covalence, wherein also the greater the number of shared electrons, the stronger the bonding.

Table 12. Metallic Bonding Strength Across Period Six: Heats of Atomization (kcal mole^{-1})

Cs	18.7	Ta	187	Ir	150	Tl	43.3
Ba	41.7	W	200	Pt	135	Pb	46.8
La	99.6	Re	186	Au	85	Bi	47.5
Hf	168	Os	160	Hg	14.7	Po	34.5

Manganese and, to a lesser degree, chromium appear to have weaker bonding than expected in comparison with their neighbors. This is consistent with the special stability of a set of exactly half-filled *d* orbitals, and suggests that electrons of such a set are not as free for general sharing.

(21) **Within a major group of the periodic table, metallic bonding strength decreases with increasing atomic radius (increasing principal quantum level of the valence electrons).**

For example, heats of atomization per g atom are, Li, 38.4; Na, 25.9; K, 21.4; Rb, 19.6; and Cs, 18.7 kcal. This is consistent with the general tendency for covalent bonds to be weaker between larger atoms, and possibly has similar cause—a weaker interaction at greater distance together with a larger number of electrons shielding the nucleus. Group II-A is exceptional in that the bonding in Ca, Sr, and Ba is all of similar strength and greater than in Mg.

(22) Within a subgroup of the periodic table, metallic bonding strength increases down the group.

For example, the heats of atomization per g atom are Ti, 112.6; Zr, 146; and Hf, 168 kcal. This is just the opposite of the major group metals. It may well be related to the differences in oxidation state stabilities between the two types of elements. Descending a major group, higher oxidation states tend to become less stable; the reverse holds for the transition metals. The increasing bonding strength down a subgroup is probably related to the increased compactness of the atoms, such that despite their difference in atomic weight and number, the lower two elements are closely similar in atomic radius. The large increase in nuclear charge without proportionate increase in radius is evidently related to higher attraction for electrons and therefore stronger bonding.

Predicting Chemical Reactions

After all the preceding preparation, how fine it would be if one could now write out a few simple, completely reliable rules for judging the direction of any chemical reaction. Unfortunately, one's judgment must depend on an intuitive understanding of a considerable number of factors, the relative contributions of which are not always easy to assess. Although such judgment is susceptible to error, it is usually reliable where it seems reasonable to attempt it; and it is certainly superior to helpless ignorance.

Of course, if the free energy of the reaction is known, there is no problem of prediction. If only the enthalpy change is known, prediction is usually valid for ordinary temperatures but much less reliable for higher temperatures. If the reaction occurs in solution and the oxidation potentials of the species involved are known, then prediction is relatively simple, and such potentials afford a rough guide for possible reactions in the absence of solvent. If the equilibrium constant is known, the relationship, $\Delta G^0 = -RH \ln K$ gives us the free energy change. But lacking such information, we must then rely on our understanding of the principles discussed in the foregoing sections.

For reactions at ordinary temperatures in which entropy changes are not expected to be large, the relative bonding strength in reactants and products may be estimated as a guide to the course of reaction. On this basis, the following rules may be useful:

(23) Reactions tend to occur wherever bond orbitals and shareable electrons are available and permit attractive interaction between atoms.

As explained in an earlier article (*3*), wherever electron sharing is possible, it occurs always with evolution of energy. We may therefore predict with confidence that all atoms possessed of external orbital vacancies will combine to the limit of their ability under prevailing conditions—whether the same or different elements are represented. The only elements whose atoms do not combine under ordinary conditions are those whose atoms contain no external low energy vacancies: the "inert" elements of the helium group. Even these, when such vacancies are created through the influence of highly electronegative elements such as fluorine, can unite by chemical bonds.

When a choice exists, then the tendency is for atoms to form the strongest bonds possible if at ordinary temperatures or at higher temperatures, to achieve the least ordered states. In predicting reactions at ordinary temperatures, we can consider the preceding principles of bond strength and attempt to decide whether the total bond strength would be greater in "reactants" or "products." On this basis we can often make an educated guess as to the probable course of the reaction.

The major types of reactions for which such predictions are most simply made are the following:

Synthesis—direct combination of elements or compounds.

Substitution—displacement of one element, or compound, from its more complex combination, by another element or compound.

Metathesis—double decomposition, or partner exchange.

Some principles of chemical reaction applicable to these types can now be discussed in some detail.

Synthesis

(24) Any two elements tend to combine if the bonds formed are stronger than the average of the bonds in the free elements.

Since nearly all elements differ in electronegativity, the bonds between two different elements are nearly always polar. As already pointed out, polar bonds tend to be stronger than nonpolar bonds. The bonds between two different elements therefore tend to be stronger than the average of the bonds in the free elements. The heats of formation of most binary compounds are therefore negative (exothermic), and in a general way, more so the greater the electronegativity difference and resultant bond polarity.

Consider, for example, the reaction of chlorine with red phosphorus. The chlorine atoms are held together in stable Cl_2 molecules requiring about 29 kcal per g atom to atomize. The phosphorus atoms are held together in giant molecule aggregates in which each atom is joined to three others by single covalent bonds of such strength that the heat of atomization is about 80 kcal per g atom. Yet these bonds are readily ruptured to form PCl_3 molecules. The heat of formation of PCl_3 is −26 kcal per equivalent. Stated a little differently, if all the phosphorus and chlorine atoms were present separately, as a gas of monatomic molecules, they might join together to form phosphorus solid and chlorine gas, or they might join together to form PCl_3 molecules. The latter process would evolve 82 kcal per equivalent whereas the former would evolve only 56 kcal per equivalent. The reaction obviously goes in the direction of forming the strongest bonds possible. But why should P—Cl bonds be stronger than P—P or Cl—Cl bonds, or their average? How do P—Cl bonds differ? The chief recognizable difference is in polarity. Chlorine is initially more electronegative than phosphorus, thus becoming partially negative (−0.10) at the expense of the phosphorus (0.30 electron). The bond length is 2.04 Å, compared to Cl—Cl of 1.98 Å and P—P of 2.28 Å. The bond polarity provides for closer interaction than expected for a nonpolar bond, and greater strength. (Some contribution from partial multiplicity is also possible here, to the extent that outer *d* orbitals of the phosphorus may be able to accommodate otherwise unused outer electron pairs on the chlorine atoms.)

Even when the atoms in the elements individually are very strongly held together, compound formation will produce still stronger bonds if they are sufficiently polar. The same factors that cause tungsten, for example, to have the highest heat of atomization of all elements enable it to form polar compounds of very high stability, so that energy lost in separating the tungsten atoms is more than regained when they combine and condense with atoms such as those of the halogens. For example, the heat evolved when tungsten and chlorine atoms unite to form solid WCl_2, 147.6 kcal per equivalent, is 19 kcal more than would be produced by combination of the same atoms to form Cl_2 and tungsten metal instead.

But when the elements are nearly alike in electronegativity, the bonds between unlike elements are low in polarity and not necessarily stronger than within the individual elements, if as strong. For example, the oxides of nitrogen are not readily formed from the elements, in comparison with which they are not very stable. The heats of formation are as follows: NO, 21.6; NO_2, 8.1; N_2O, 19.5; N_2O_3, 20.0; N_2O_4, 2.3; and N_2O_5, 3.6 kcal/mole. These positive heats do not mean that energy is not released when the N—O bonds are formed, but merely that the energy released is not sufficient to break up the strong bonding in N_2 and O_2. As also pointed out earlier, bonds of low polarity between atoms quite different in size are weaker, and this too may be a factor in determining whether a synthesis will occur spontaneously. For example, the H—Te bond is essentially nonpolar and relatively weak (average bond energy 57 kcal) because of the size difference. Formation of H_2Te from the elements is therefore not favored, but would absorb 37 kcal per mole. On the other hand, the C—H bond is very strong (average in CH_4, 99.5 kcal), more than enough to compensate for the energy required to break apart the H_2 molecule and atomize graphite.

(25) **Two molecules or ions tend to combine if an outer electron pair of one can be shared with another having an outer vacant orbital.**

A very large number of reactions of this type are known. They include the direct formation of all molecular addition compounds, the uniting of two simple compounds to form a complex compound, and addition polymerization (the type that occurs by addition of molecules together, without splitting out any other products). Principles governing the relative stability of such combinations have already been discussed and will not be detailed here. However, some illustrations may be of interest:

$$CaO + SO_3 \rightarrow CaSO_4$$

Calcium oxide is itself a very stable substance, with a heat of atomization of 254 kcal per mole, and one might well wonder why it should react further with anything. But by having a relatively high partial negative charge, the oxygen of calcium oxide is a good potential donor. The three oxygens attached to sulfur have withdrawn electrons from the sulfur, not enough to give them donating ability but enough to expose the sulfur nucleus to the electrons of the calcium oxide oxygen. Consequently this negative oxygen becomes coordinated to the sulfur, forming the sulfate. The standard heat of formation of $CaSO_4$ is 342 kcal per mole, in contrast to those of CaO, 152, and SO_3, 95, the sum of which is only 247 kcal.

In general all oxides in which the oxygen is sufficiently negative to make it effective as donor tend to join all oxides in which an available orbital or more can act as acceptor. The acceptor must, however, have a higher attraction for electrons than has the positive atom of the donor oxide, or nothing would be gained by the reaction. We would not, for example, expect the sodium (charge, 0.40) in Na_2O to accept electrons from the oxygen in CaO because the calcium (0.57) would attract them more strongly. Furthermore, we would not expect two oxides such as N_2O_5 and SO_3 to combine because in neither is the oxygen sufficiently negative to donate effectively.

Finally, it is recognized that amphoteric oxides such as water may be able to react as either donor or acceptor, depending on the character of the other oxide.

Analogous reactions occur between halides (especially fluorides) and sulfides of metals and those of nonmetals, forming complex halides and sulfides.

$$CaCl_2 + 6H_2O \rightarrow CaCl_2 \cdot 6H_2O$$

This kind of reaction depends on the ability of water oxygen to donate electrons better than does a chloride ion, presumably a result of the higher concentration of an electron pair on oxygen than on chloride ion. The water molecules can thus become coordinated to the calcium ion. A similar reaction does not occur with KCl because the potassium, with its larger size and lower nuclear charge, is less effective as an attractor of electrons.

$$x\ C_2H_4 \rightarrow (C_2H_4)_x$$

Here the joining together of molecules is made possible by the fact that neither the valence electrons nor the orbitals can be used to maximum capacity in an olefinic double bond. Various explanations might be offered. Perhaps the easiest to visualize is the inability of two orbitals of the same carbon to be oriented toward the other carbon at the same time. Or we may consider the problem of trying to concentrate more than one pair of electrons within the space between the two carbon atoms. Two single bonds appropriately directed to minimize repulsions are then expected to provide greater stability than one double bond. The approximate bond energies are 147 kcal per mole for an olefinic double bond and 164 kcal for the equivalent in two single C—C bonds. Two single bonds thus impart greater stability than one double bond.

This properly calls attention to the question of whether all unsaturated molecules polymerize, and if not, why not. We are at once confronted with CO_2 which does not polymerize, with ketones which do but by condensation (splitting out water) rather than direct addition, with aldehydes which under certain conditions can polymerize by addition as well as by condensation, and by silicon dioxide and the silicones that exist only as polymers. Bond energy values that indicate approximately the strengths of C—O single and double bonds are 81–4 and 164–74.

A system in which each carbon atom is joined by double bonds to two oxygen atoms thus seems approximately equal in stability to one in which each carbon is connected to four oxygens by single bonds and each oxygen joined to two carbons. This is quite unexpected, however, because in general two single covalent bonds should be stronger than one double bond, other factors being equal. Carbon dioxide is apparently exceptional among a large number of double bonded compounds capable of addition to form polymers; the average bond energy in CO_2 is 192 kcal, or 20–30 kcal more than for a carbonyl bond.

All synthesis and addition reactions occur with a decrease in entropy, and therefore become less able to occur with increasing temperatures. At high temperatures where the entropy term exceeds the enthalpy change, the opposite or decomposition reactions are favored.

Substitution

(26) **An element tends to displace another from a compound if a more polar bond results.**

This relationship between bond polarity and bond strength can be used only as a rough approximation because it neglects other factors such as bond order and bond length, as previously discussed. However, it is useful as such, since in many instances other factors do not vary widely. In particular, highly electronegative elements exhibit a strong tendency to acquire negative charge, and if they have not been very successful in one combination, they tend to leave it in favor of another combination in which they can acquire higher negative charge. As stated, the principle describes the tendency of a highly electronegative element to displace a less electronegative element from its compound with an electron source. This is illustrated by the familiar halogen displacement series; heats of formation always increase for comparable halides of a given element in the order $I < Br < Cl < F$. It is further illustrated by the ready conversion of hydrides, sulfides, bromides, nitrides, and iodides to oxides by heating in air.

Indirectly, the principle describes the displacement of a less active metal by a more active metal. For example, sodium will displace aluminum from its chloride and, much more readily, hydrogen from water. But this only seems to imply a deliberate, positive action of sodium. It may more accurately be recognized as a manifestation of the tendency of chlorine and oxygen to acquire higher negative charge.

Metathesis

(27) **The major tendency is for metathetical reactions to favor the formation of the most polar bond possible.**

This is because the most polar bond is usually the strongest bond. It must be recognized at once, however, that (1) the most polar bond is not necessarily the strongest although it often is, and (2) the reaction does not necessarily favor the strongest bond or most stable compound, because free energy can sometimes be released when a very stable and a less stable compound interchange to form two new compounds of intermediate stability but above the average of the reactants.

Yet this rule is a very useful one despite its limitations, for it applies to many of the more important kinds of chemical change. Some examples are:

The synthesis of organometallic compounds from halides of more electronegative metals and organo compounds of more active metals.

$$HgCl_2 + 2CH_3MgCl \rightarrow Hg(CH_3)_2 + 2MgCl_2$$

The most polar bonds here are those between Mg and Cl, the charge on Cl being -0.17 in $HgCl_2$ and -0.34 in $MgCl_2$.

Hydrolysis of binary compounds in general, of nonmetal with less electronegative nonmetal or metal.

$$NaH + H_2O \rightarrow H_2 + NaOH$$

Here oxygen is the most electronegative element and becomes much more negative in OH^- (-0.67) than it was in H_2O (-0.25).

$$Mg_3N_2 + 6H_2O \rightarrow 2NH_3 + 3Mg(OH)_2$$

Here the Mg—O bond is most polar.

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Kinetics—Early and Often

Most chemists agree that the measuring and understanding of the rates of chemical reactions and the mechanism by which they occur are important activities in chemistry. It is therefore somewhat surprising that any reasonable discussion of these areas is normally deferred until the third or fourth year of college. Rates may be mentioned in first year chemistry courses, such as are given in high schools, and the effect of concentration and temperature generalized. But the impression is almost always given that a study of the equation for the net reaction provides evidence for the factors which will affect the rate and that the equation will enable one to predict from it which concentrations will have what effect on the rate.

Chemistry, at these early stages, almost always concerns itself with the nature of the products and the reactants and with the equilibrium between them. But it very seldom deals with that interesting phase of chemistry (represented by the equal sign) through which the reactants do indeed become the products. Rate experiments, when performed, usually corroborate the erroneous idea that the net reaction is intimately related to the rate equation, either by presenting only qualitative evidence as to the effect of concentration, or by dealing with systems in which the mechanism is so simple that there is a pseudo-correspondence between the net reaction and the rate equation. Even when rates and mechanism finally are approached at a higher level, they are seldom dealt with on an experimental basis so that few of the interesting features of mechanisms are met in the laboratory.

There has been considerable justification for this approach in the past when the mechanisms of very few reactions have been completely understood, when rate data have been hard to obtain, and when the majority of chemists have actually been more interested in other areas. None of these "rate determining factors" seems, however, to be effective now.

The studies of rates and mechanisms in chemical reactions has now become central to the understanding of chemistry. Thus, it seems most important to introduce a reasonable discussion of these ideas in the earliest course in chemistry and to reinforce these ideas in each subsequent course, basing the approach as firmly as possible on experimental observations directly accessible to the student.

Let me first list the areas which seem to be important for a minimally educated college graduate (not necessarily a chemist) to have understood in connection with rates and mechanisms and then outline possible sequences by which the total picture might be achieved in the mind of the student. I would choose to classify these ideas into three main categories:

The variables which ordinarily affect the rate of chemical reaction.

The mechanism by which the chemical reaction actually occurs.

The relationship of this mechanism to the equilibrium.

In order to approach most directly the relationship of the variables affecting rate, it seems feasible first to study the rate and to determine experimentally the rate equation. In such an equation the rate of change of some concentration is expressed as a function of certain concentrations and, at any given temperature, a constant. For example,

$$d[\mathrm{HBr}]/dt = k\,[\mathrm{H_2}]\,[\mathrm{Br_2}]^{1/2}$$

for the initial stage of the net reaction

$$\mathrm{H_2 + Br_2 \rightarrow 2HBr}$$

In some cases this differential rate equation can be integrated to give an expression for the concentration of each variable as a function of time and the additional concentrations. For example,

$$\log\,(\text{ester}) = kt + C$$

for the net reaction

$$\mathrm{H_2O + CH_3COOC_2H_5 \rightarrow CH_3COOH + C_2H_5OH}$$

It is interesting to observe that there is no general relation between either the differential or integrated form of the rate equation and the equation for the net reaction. In many cases the rate of reaction is unaffected by changes in concentrations of some of the reactions. For

$$\mathrm{2NH_3}(g) \rightarrow \mathrm{N_2}(g) + \mathrm{3H_2}(g)$$

on a tungsten surface the rate is independent of the concentration of ammonia. In many other cases the concentrations of substances appear in the rate equation whereas these substances do not appear in the equation for the net reaction. The rate of the net reaction

$$\mathrm{C_{12}H_{22}O_{11} + H_2O \rightarrow 2\ C_6H_{12}O_6}$$

in dilute acid is given by

$$d[\mathrm{C_{12}H_{22}O_{11}}]/dt = k[\mathrm{C_{12}H_{22}O_{11}}]\,[\mathrm{H^+}]$$

Furthermore, there is no general correlation between the exponent of each concentration, or the form in which it appears in the rate equation, and the coefficient of the corresponding substance in the equation for the net reaction. Thus, the general rate equation is

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Presented as part of the Symposium on Kinetics in the Undergraduate Curriculum before the Division of Chemical Education at the 144th Meeting of the American Chemical Society, Los Angeles, California, April, 1963.

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k_1[\mathrm{H_2}]\,[\mathrm{Br_2}]^{1/2}}{k_2 + [\mathrm{HBr}]/[\mathrm{Br_2}]}$$

for the net reaction

$$\mathrm{H_2} + \mathrm{Br_2} \rightarrow 2\mathrm{HBr}$$

This comparison of experimental net equations and experimental rate equations quickly leads to the conclusion that any correlation between the two must be quite coincidental or, at least, very well hidden by the intricacies of any relationship.

The effect of temperature on the constant in the rate equation is often experimentally calculable since, in general

$$\frac{d \log k}{d[1/T]} = \frac{\Delta H_{\text{activation}}}{\mathrm{R}}$$

A plot of the logarithm of the rate constant versus the reciprocal of the absolute temperature commonly approximates a straight line from whose slope k may be calculated.

No variables other than certain concentrations and the absolute temperature are ordinarily found to affect the rate of a given chemical reaction.

It is quite true that there are reactions, particularly those occurring on solid surfaces, where it is extremely difficult to express the concentration. But it is commonly accepted in these cases that the difficulty is in defining the concentration rather than being based on a new kind of variable.

It is, of course, quite possible to interpret these concentration and temperature variables in terms of various theories, but I will leave the discussion of such theories to the authors of other papers and adhere here to a discussion of some experimental observations with minimum reference to collision or activated complex theory as such.

Mechanism of Chemical Reactions

A major principle for the understanding of the mechanism of chemical reactions is committment to the idea that all mechanisms are possible, but that some mechanisms proceed more rapidly than others, and that normally the observed rates are determined by a single mechanism—that which is most rapid. Many systems are known in which simultaneous or parallel reactions occur, but many others can be adequately treated in terms of a single predominating mechanism.

In a typical predominating mechanism many steps may occur. These always, of course, involve the collision of certain reacting molecules and the formation of intermediate molecules. The intermediate molecules then continue to react in further steps of the reaction to produce the final products. Some reactions involve very complicated mechanisms and others relatively simple mechanisms, but in many cases the overall rate of the reaction is primarily determined by the rate of a single step known as the slow step of the reaction mechanism. When there is a single slow step the experimentally determined rate equation and the experimental dependence of the rate constant on absolute temperature turn out to be especially simple.

Finally, in the mechanisms of many chemical reactions the intermediate products are highly reactive and can exist only at small concentrations. In many cases, these concentrations build up as the reaction begins to a level which remains quite constant during the major course of the reaction. Such concentrations are said to experience a *steady state*. Substances having a steady state concentration are being formed and reacting at the same rate so that their net concentration at any time is constant.

Thus, one writes down various plausible mechanisms and compares the rate equation calculated from the assumed mechanism with the experimental one. Often only one mechanism is found which gives concurrence with rate and other (e.g., energetic) data. Such a mechanism is, then, assumed to be correct.

Equilibrium and Kinetics

Once the general mechanism of a reaction is understood, it is easy to demonstrate, by applying the principal of micro reversibility, that the equilibrium state involves a set of simultaneous reactions in which every step in the mechanism is proceeding in both directions at equal rates. It is also easy under these conditions to show the relationship of the rate expressions to the equation for the net reaction. The sum of all of the mechanistic steps must give the equation for the net reaction. Ordinarily the equation for the rate of reaction, if there is a single slow step, depends only on the concentration of the reactants in that slow step and on the absolute temperature of the system.

Applicability of Mechanistic Ideas in Early Chemistry

It is difficult to see why the ideas presented above which summarize most of the major points important in understanding rates and mechanisms of reaction cannot be presented at a much earlier stage than is now done. It further seems possible that presenting such ideas at an early stage would allow students to have a new comprehension of what actually occurs in chemical reactions and, thus, a much better understanding of the nature of chemicals and their interactions with one another. The problem remains to devise experimental methods of illustrating these ideas. It seems especially important to devise experiments which the students can themselves perform and from which these ideas become dramatically underlined. May I therefore suggest at least one experiment which seems to fulfill some of these criteria.

The "Blue Bottle" Experiment

Let us consider a chemical system which is very easily constructed and on which very simple experiments can be done by students with a minimal experience in chemistry.[1] I have used this experiment with students from the 7th grade through graduate school with considerable success at all levels. Even faculty members seem to be pleased with the observations and conclusions which can be made in connection with it. The system normally consists of a glass flask approximately half full of a clear colorless liquid with a rubber stopper in the top. Shaking the flask causes the liquid to turn blue. Upon standing the blue liquid reverts to its original colorless condition. Shaking initiates a further bluing, then de-bluing cycle. Students of all degrees of sophistication seem to enjoy suggesting interpretations of these observations. It is commonly suggested that there is a colored material on the stopper or that the increased contact with the glass on shaking causes the color change. These ideas are readily checked experimentally by up-ending the flask or by gently swirling it so that the liquid does cover the glass or touches the stopper. In neither case does the blue coloration appear.

Perhaps the most obvious change in the flask upon shaking is that the kinetic energy of the contents is increased. This leads to the idea that the rise in temperature causes the blue color with the subsequent loss in heat as the flask cools back to room temperature allowing the color to revert. Again this can be readily checked experimentally by warming the flask in one's hands and showing that the blue coloration does not occur.

The common suggestion at this point is that there are two layers which are mixed when the flask is shaken and then settle out. This can be quickly checked by again up-ending the flask and noticing that the blue color disappears uniformly in the long cylindrical neck rather than rising or falling as would be true were there two layers which were separating. A similar suggestion is that shaking may mix any gas which is in the top of the flask with the liquid and that upon standing the gas separates from the solution again. This can also be experimentally checked just as the earlier two layer theory, since it is only a special case of it. Again the uniform disappearance of blue color throughout the flask indicates that this suggestion is not acceptable. Note that each suggestion fits all the observations made up to that point, but can be shown to be inadequate to fit further possible observations.

Once the idea that there may be a gas in the top of the flask arises, it becomes apparent that this may indeed be a reactant which does not later escape from the solution. Students quickly suggest various ways of checking this theory. Assuming that the gas pressure was originally atmospheric this pressure should have dropped and gentle removal of the stopper should show bubbles in the inside of the "liquid seal" around the stopper. It is wise to point out at this time that this may seriously affect the experiment by contaminating the contents of the flask with air. However, the experimental check does indeed show that the pressure is less than atmospheric and further shaking will again reduce the pressure below atmospheric. An even more clever way of checking the possibility that a gas is entering the liquid and causing the blue color is to observe the interface between gas and liquid. If the theory is correct there should be a thin blue layer where the mixing is continually occurring. Close examination shows this layer. The fact that the layer is not

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[1] I found this experiment at the University of Wisconsin in 1954, but heard it was discovered at Cal Tech.

Clitheroe Royal Grammar School for Boys
York Street
Clitheroe, Lancashire
July 10, 1963

Dear Professor Campbell,

Following your lecture on "Chemical Study" at University College, London a week ago, and the few minutes conversation we had at the Middlesex Hospital Medical School, I yesterday gave a small group (seven) of my boys a flask with the methylene blue (caustic soda) glucose solution and asked them to deduce as much as they could about the chemistry of the system from what they could observe, without the use of any other reagents. They are all aged 18 and have just attempted "A" level chemistry. They were given no help or suggestions by me. One boy acted as "scribe" for the group and I enclose his rough notes (in red) and his report (in blue). The first side of the (blue) was done at the time of observation; the remainder was done after 24 hours thought by the boys. The train of reasoning is fairly clear (and it is interesting to note that at one time they thought the liquid had three reactive components X, Y, and Z).

Norman Thorpe
Senior Chemistry Master

(Red) notes from students

$$\text{Air} + \text{liquid} \xrightarrow{\text{fairly slow}} \text{Blue cpd} + (?)$$

$$(?) + \text{Something in liquid} \xrightarrow{\text{possibly fast or very slow}} \text{X}$$

$$\text{X} + \text{Blue cpd} \xrightarrow{\text{possibly very slow or fast}} \text{Liquid} + \underset{\text{colorless}}{\text{new cpd}}$$

$$\text{Air} + \text{Something in liquid} \xrightarrow{\text{overall}} \text{new cpd}$$

Liquid contains X and Y

$$\text{Gas} + \text{X} \xrightarrow{\text{fairly slow}} \text{blue cpd} + (?)$$

$$(?) + \text{Y} \rightarrow \text{Z (another cpd)}$$

$$\text{Z} + \text{Blue cpd} \rightarrow \text{X} + \underset{\text{colorless}}{\text{new cpd}}$$

$$\text{Gas} + \underset{\text{catalyst}}{\text{(1 component)}} \rightarrow \text{blue cpd}$$

$$\text{Blue cpd} + 2\ \text{comp} \rightarrow \text{new cpd} + 1\ \text{component}$$

thick coincides with the observation that the blue color disappears on standing. So, in the case of the surface layer, the blue color disappears as it diffuses into the bulk liquid. A further quick check can be run by replacing whatever gas is in the flask, normally air, by natural gas. Shaking the liquid with natural gas does not cause any blue coloration. Replacing the natural gas with air and repeating the shaking again causes the blue coloration which disappears on standing. One now has fairly conclusive evidence that some ingredient of air does indeed react with the liquid to form the blue solution.

By this time one will almost certainly have observed that the rate of the initial "bluing reaction," while not instantaneous, is quite rapid, occurring in a few seconds, whereas the disappearance of the blue color takes much longer depending on the conditions but approximating twenty seconds or so. This allows the tentative conclusion that there must be at least three reactions occurring in the flask. There is the solution of the gas in the liquid phase, followed by a reaction with something in the liquid to form the blue color, followed in turn by the reaction of the blue material to produce colorless products. We can tentatively represent this reaction mechanism (note that the student has arrived at this mechanism without any knowledge of the chemical ingredients of the flask and on the basis of very simple observations which can be made in any classroom) by the following scheme:

$$\begin{aligned} A(g) &\rightarrow A(soln) \\ A(soln) + X &\rightarrow B \\ B + Y &\rightarrow \text{products} \end{aligned}$$

Suggested mechanism 1

In this scheme A represents the original gas; B represents the blue material; X represents the reactant which converts the gas to the blue material, B; and Y represents the substance which reacts with B, the blue material, to give colorless products. It is interesting to note that essentially every group with whom I have discussed this experiment has arrived at this mechanism without very much prompting. The question now reads: Is the mechanism adequate to interpret all the experimental evidence? The answer is that it does indeed interpret all the experimental evidence observed so far by most of the people, but not all of the experimental observations which actually can be made. For example, perspicacious students will already have noticed that the length of time the solution remains blue depends on how long one shakes the flask. Very few will havé specifically noted that it is also true that the intensity of the blue color is independent of how long the flask is shaken. These two bits of information, however, are readily observed and prove to be very important in continuing a study of the mechanism.

It is relatively easy to show, with an approximation to quantitative measurements, that the length of time the solution stays blue is directly proportional to the degree of shaking. One shake may cause blue color for ten seconds, two shakes for about twenty seconds, four shakes for about forty seconds and so on. Thus, the time the flask stays blue depends directly on the time of shaking. This is certainly consistent with the first step in the reaction scheme above in that one would expect more gas to dissolve if one shook longer. It is not readily consistent, however, with the second step. One might guess, if one increased the concentration of dissolved gas that the second step of the reaction would

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(Blue) notes from students

Examination of the contents of a flask

Shakes given to flask	Time to return to original color (sec)
1	10
2	15
3	20
4	25
5	30

On shaking, the solution turned blue, the intensity of the colour depending on the time shaken. The blue colour then faded back to the original colour.

The experiment was repeated in the dark. The times were the same showing that the solution is not light sensitive.

The apparent suspension in the liquid always remained white.

On removing the bung, air was heard to enter the flask. This suggests that some of the gas is permanently absorbed. This is confirmed by a permanent blue colouration which remains round the meniscus of the liquid. On tilting the flask a permanent ring appeared on the glass of the flask, corresponding to the meniscus of the liquid. On placing a glass stirring rod in the solution the blue ring formed around it. This suggests possibly that the glass is catalyzing the reaction.

The reasoning was then continued 24 hours later.

The first thought was that a reversible reaction was taking place. Since however the pressure is reduced inside the flask this theory is not altogether true. This reduction in pressure might be attributed to the gas absorbed on the surface (the blue colour shows this) but if the surface absorbs the gas, why does not the whole solution absorb gas. This leads us to think that the first reaction is one in which the gas is absorbed by the liquid. The equation for this step might be.

$$\text{gas} + \text{first component of solution} \rightarrow \text{blue compound}$$

This is a fairly slow reaction. The blue compound then reacts with another component of the solution.

$$\text{blue compound} + \text{second component of solution} \rightarrow \text{new compound (colourless)} + \text{first component of solution}$$

This is a very slow reaction.

The overall equation is

$$\text{Gas} + \text{second component of solution} \rightarrow \text{new compound}$$

It would thus appear that one component of the solution is acting as a catalyst.

The slight blue colouration on the surface of the liquid is explained as follows: The gas reacts with the surface of the liquid to form the blue compound. The blue compound then reacts with the second component to form the new compound. Hence the second component near the surface of the liquid is all reacted and hence the blue colouration is permanent.

Conclusion

It would appear that the reaction taking place is of the general form

$$\underset{\text{catalyst}}{A} + B \rightarrow \underset{\text{addition compound}}{AB}$$

$$AB + C \rightarrow AC + \underset{\text{catalyst}}{B}$$

proceed more rapidly and that increasing the initial concentration of dissolved gas by a factor of four would not cause the reaction to take four times as long. The time would certainly increase as there is more gas to remove, but it should not increase four times. Furthermore, the fact that the blue color lasts longer as the concentration of dissolved gas is increased is not directly consistent with the fact that, even though the concentration of dissolved gas may have increased, the intensity of the blue color, which apparently measures the concentration of an intermediate substance, does not increase. As a matter of fact, the constant level of the blue color would indicate that the concentration of this intermediate rather quickly reaches a steady state which is maintained throughout the body of the reaction, rather quickly dropping from a steady state value to zero as the de-bluing reaction nears completion.

How do we account for the lengthening of the time the system stays blue, while simultaneously accounting for the constant intensity of the blue color regardless of the concentration of dissolved gas?

At this point, students typically suggest many possible alternatives which can be explored experimentally. The weight and amount of experimental evidence is now so great that it is relatively easy to discard most of the theories which are presented. One theory which is not so readily discarded, however, is that X is actually a limiting reagent in the second step of the mechanism above. Perhaps increasing the concentration of dissolved gas cannot give any more blue color than can be formed from the limiting amount of ingredient X. It rather quickly follows from this hypothesis that if the blue color is to remain constant and yet be reacting in step three, X must be regenerated in step three and be a product. This is consistent with the observed fast rate of the second reaction and slow rate of the third. Thus, we might modify reaction three above to read:

$$\mathrm{B} + \mathrm{Y} \xrightarrow{\text{slow}} \mathrm{X}$$

We now have a scheme which fits all the observations made so far. The constant level of blue color is reached because X is a limiting reagent which reacts rapidly with the dissolved gas forming the blue intermediate. The blue intermediate slowly reacts with Y regenerating X which quickly forms more blue intermediate by reacting with further dissolved gas. As the dissolved gas is completely used up, X remains in its colorless state and no more blue intermediate can be formed.

We now have a scheme which is consistent with all the observations which can be readily made merely by shaking the flask. However, we have not exhausted the possibilities which the system offers for exploration. For example, adding the three steps does not give a net reaction!

$$\begin{array}{ll}
\mathrm{A}(g) \xrightarrow{\text{fast}} \mathrm{A}\ (soln) & \\
\mathrm{A}(soln) + \mathrm{X} \xrightarrow{\text{fast}} \mathrm{B} & \text{Suggested mechanism 2} \\
\mathrm{B} + \mathrm{Y} \xrightarrow{\text{slow}} \mathrm{X} & \\
\hline
\text{Net: } \mathrm{A}(g) + \mathrm{Y} \longrightarrow ? &
\end{array}$$

No product is listed. This can be corrected by using scheme 3.

$$\begin{array}{ll}
\mathrm{A}(g) \xrightarrow{\text{fast}} \mathrm{A}(soln) & \\
\mathrm{A}(soln) + \mathrm{X} \xrightarrow{\text{fast}} \mathrm{B} & \text{Suggested mechanism 3} \\
\mathrm{B} + \mathrm{Y} \xrightarrow{\text{slow}} \mathrm{X} + \text{products} & \\
\hline
\text{Net: } \mathrm{A}(g) + \mathrm{Y} \rightarrow \text{products} &
\end{array}$$

It is now possible to explore the effect of concentration on the rates of reaction. Since one does not know the chemical contents this can be done most readily by adding water to the flask. To the surprise of most students, the addition of water turns the contents of the flask blue. This surprise is rather quickly resolved when one remembers that there is dissolved air in water, and that it is this dissolved air which is almost certainly causing the blue. (As a matter of fact, this experiment turns out to be a rather good method for analyzing for dissolved air (oxygen) in waters and can be calibrated to give rather accurate and reproducible results.) Once the blue color caused by the added water has disappeared, one does indeed find that the rate of the de-bluing reaction has decreased, in fact it has decreased rather markedly. Another effect of decreasing the concentration of X is that the intensity of the blue color decreases, consistent with our mechanism. Thus, the concentration of X, and hence B, will have decreased by adding the water as well as the concentration of Y. The effect of decreasing the concentrations of B and Y, since they react in the slow step in the mechanism is that the overall mechanism slows down as observed. One might predict therefore that doubling the volume by adding an equal volume of water would decrease the rate of the slow reaction by a factor of four, since both B and Y decrease by a factor of 2 in concentration. Actually the rate drops more than this indicating that there is a complication of the mechanism not yet anticipated.

By this time, students will probably have noted that the solution is slippery. This indicates that it is probably basic. Since it is basic it may well be that the presence of base has some effect on the reaction mechanism. This is actually the final clue which is needed completely to unravel the mechanism because it is true that although hydroxide ion does not react in the rate determining step nor in the net reaction (as is true of B also), it is important in determining the overall rate of reaction. We thus find that the experimental rate equation for this reaction is

$$\frac{d[\mathrm{B}]}{dt} = k[\mathrm{B}]\,[\mathrm{Y}]\,[\mathrm{OH}^-]$$

Note that it is impossible, as is generally true, to guess the rate equation from the equation for the net reaction

$$\mathrm{A} + \mathrm{Y} \rightarrow \text{products}$$

Also note that the only chemical we have identified so far is hydroxide ion.

However, even without identifying the chemicals it is possible to study the effect of temperature on the rate of reaction by plotting the logarithm of the de-bluing time for a constant amount of dissolved gas as a function of the reciprocal of the absolute temperature, $1/T$. This is possible, because the rate of the slow step is independent of the concentration of oxygen and thus the time, t, it takes the total oxygen to disappear is directly related to the rate constant k. A straight line is obtained from a log t versus $(1/T)$ plot. (From this one can of course obtain the activation energy for the slow step.)

The actual system can be made up in a very rough fashion, but should contain approximately 20 g of sodium hydroxide, 20 g of glucose (reactant Y), and perhaps half a milliliter of 1% alcoholic methylene blue (reactant X) solution per liter of water. There is nothing very critical about these reactants and they need not be weighed out. It then becomes apparent that the system involves the oxidation of glucose by oxygen (reactant A) catalyzed by methylene blue.

Even without identifying the chemicals, it is possible for students to see that ingredient X is a catalyst for the reaction, since it is consumed and then regenerated in the reaction. Thus X appears in the rate equation but does not appear in the equation for the net reaction. This system is one of the few in which the intermediate molecule formed by the catalyst is actually visible. Thus, the system provides valuable support to any discussion of the nature of catalytic action.

The role of hydroxide ion is somewht more difficult to see and cannot be deciphered completely without a knowledge of the ingredients involved. The actual role of the hydroxide ion is to convert glucose, G (formerly called reactant Y), to the glucoside ion, G^-, in a rapidly reversible equilibrium. It is apparently the glucoside ion which is involved in the actual rate determining step.

$$\begin{array}{lll}
1. & G + OH^- \overset{\text{fast}}{\rightleftharpoons} G^- + H_2O & \\
2. & A(g) \xrightarrow{\text{fast}} A(soln) & \text{Suggested} \\
3. & A(soln) + X \xrightarrow{\text{fast}} B & \text{mechanism 4} \\
4. & \underline{B + G^- \xrightarrow{\text{slow}} X + \text{products}} & \\
 & \text{Net: } G + A(g) \longrightarrow \text{products} &
\end{array}$$

The introduction of the equilibrium constant for the rapid reversible equilibrium allows one to show, however, that the rate can be expressed in terms of glucose concentration and hydroxide concentration, as we found experimentally to be the case.

Thus, for the slow step (and hence the whole mechanism)

$$\frac{d[B]}{dt} = k_4[B]\,[G^-]$$

where B is the oxidized (blue) form of methylene blue. But

$$K_{eq_1} = \frac{[G^-]}{[G]\,[OH^-]}$$

$$[G^-] = K_{eq_1}[G]\,[OH^-]$$

$$\frac{d[B]}{dt} = k_4K_{eq_1}[G]\,[OH^-]\,[B] = k[G]\,[OH^-]\,[B] = k\,[\text{glucose}]\,[OH^-]\,[\text{methylene blue}]$$

which agrees completely with the experimentally determined rate equation. Note the reaction is zero order in oxygen, the gas A, from the air.

It is now interesting to note that we have indeed introduced, with a very simple system, and very simple observations, most of the important ideas concerning the mechanism and rates of chemical reactions which it is normally considered a student entering graduate school should have. And we have done this at the level of a first course in chemistry. One can also point out that the reaction is susceptible to quantitative measurements in a laboratory. In terms of these quantitative measurements and an actual knowledge of the ingredients, it is quite possible for the student to gain great insight into the effect of changing concentrations or temperature on a reaction mechanism.

It is further profitable to point out to the student the analogy between the role of methylene blue in the oxidation of glucose in this system and that of hemoglobin in physiological systems where glucose is oxidized. Students prove to be quite interested also in the tie-in with the use of methylene blue as an antidote for carbon monoxide poisoning in the blood, and the mechanism of its action.

Kinetics—Early and Often

It is for reasons such as those presented above that the Chemical Education Material Study has made a serious effort to introduce the major ideas concerning rates of reaction and reaction mechanism in a clear and correct fashion in a first course in chemistry. It is for the same reason that we at Harvey Mudd College have introduced kinetic experiments at all levels from the freshman year on.

What is needed now are further reactions which illustrate, as clearly as the methylene blue, the various aspects of mechanisms. Particularly needed are some reactions whose rates can be readily measured, for which he rate equation can be directly determined, and for which it is obvious that the rate equation and the equation for the net reaction are unrelated in any simple fashion. The usual rate experiments (such as the iodine clock, hydrogen peroxide decomposition, inversion of sucrose) do not, unfortunately, meet these criteria. Even the reaction between silver ion and formate ion has the unfortunate property of possessing a rate equation which corresponds ostensibly to the equation for the net reaction. There are, of course, reactions known which do not have these drawbacks, but a larger number need to get into the literature of undergraduate experiments, and it is hoped that those knowing such experiments will see that this happens.

The field of reaction rates and mechanisms is far too important to be slighted in the future as it has been in the past. Experiments can be done, even in a first course in chemistry, which are intelligible to the student and which clearly point out the real effects of concentration and temperature. The complicated series of steps—with each step simple—which give the overall mechanism and the relationship of the reaction mechanism to the equilibrium state can also be deduced from experimental data. "Kinetics—Early and Often," ought to produce interesting results in the education of future chemists.

Section 7 Reactions in aqueous solutions

The importance of energetics (lattice energies, solvation energies, entropy changes etc.) is again stressed in the article by A. G. Sharpe. J. C. Fairbank shows how the Lowry-Bronsted theory of acids and bases can be introduced into school courses. (A paper of similar content by F. M. Hall is: "The Theory of Acids and Bases", *Education in Chemistry*, 1964, p. 91.) J. Serre reviews with clarity the structures of ammonia and the ammonium ion and their interactions with solvent molecules.

A great difficulty in teaching electrochemistry has been confusion over sign conventions and nomenclature. The article by P. van Rysselberghe gives an authoritative account of the conventions recommended by IUPAC for general adoption.

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SOLUBILITY EXPLAINED

By A. G. Sharpe, M.A., PH.D., F.R.I.C.

Lecturer in Inorganic Chemistry, Cambridge University

A *solution* is a homogeneous mixture of two (or more) components. In this context, homogeneity denotes not merely uniformity under observation by the eye, but incapability of separation into constituents by any mechanical means: in a true solution the particles of both constituents are separate molecules or ions, though there is sometimes quite strong interaction between one molecule or ion and a small number of others in its immediate environment. It is common practice to discuss solubility in terms of a solvent and one (or more) solutes: the *solvent* is the component that dissolves the *solute*, *i.e.* retains its own physical state after addition of the solute. In some instances, however, it is not clear which component is the solvent and which the solute. Such a case exists for two liquids such as ethanol and water, which are miscible in all proportions: the distinction is of no real importance in these circumstances, but it is conventional to refer to the component present in greater amount as the solvent.

Solutions are often classified on the basis of their physical state (gaseous, liquid, or solid) and the physical state of the pure solute at the ordinary temperature. There are then nine types of solution, and these are listed, with an example of each, in the table.

Types of Solution

Solution	Example
Gas in gas	Air
Liquid in gas	Water (vapour) in nitrogen
Solid in gas	Iodine (vapour) in nitrogen
Gas in liquid	Carbon dioxide in water (soda-water)
Liquid in liquid	Ethanol in water
Solid in liquid	Sodium chloride in water
Gas in solid	Hydrogen in palladium
Liquid in solid	Mercury in silver (amalgam)
Solid in solid	Copper in nickel (coinage alloy)

This article is concerned mainly with solutions of gases, liquids and different types of solid in liquids, since these are the solutions with which the chemist, especially in the early stages of his training, is most concerned. The general principles on which solubility is discussed apply, however, to all types of solution, and the aim of this account is to provide a brief introduction which, although reasonably self-contained, will serve as an introduction to a more advanced understanding of the whole field of solubility. No part of this, it is interesting to note, is more difficult to treat quantitatively than the solubility of salts in water, the subject with which the student usually makes his first acquaintance with solubility phenomena.

Most pairs of substances (other than pairs of gases) are only partially miscible. When sucrose (ordinary sugar) is stirred with water at 25°, for example, the concentration of the solution eventually reaches a constant value: the solution is then said to be *saturated*, and its concentration is the *solubility* of sucrose in water at this temperature. This solubility may be expressed in several ways. From a physicochemical viewpoint, the most fundamental of these is in terms of the ratio of the number of gram-molecules, or moles, of sucrose to the total number of gram-molecules (of sucrose and water) in the liquid phase—*the mole fraction* of sucrose. Also in common use are *molarity* (the number of moles per litre of solution), *molality* (number of moles per 1,000 g of solvent) and *weight per cent* (number of grams of solute per 100 g of solution) as units of solubility: the second of these is especially widely used in dealing with solutions of electrolytes, where the term 'gram-formula-weight' replaces 'gram-molecule.' For solutions of gases in liquids the absorption coefficient (the volume of gas, reduced to 0 C at 1 atm, dissolved by one volume of solvent at the temperature of the experiment under a partial pressure of the gas of 1 atm) is the unit most frequently employed.

The equilibrium which exists in a saturated solution is, like all other equilibria, a dynamic one, as may be shown by isotopic tracer experiments: the rate of dissolution of the solute is equal to its rate of separation from the solution. The position of equilibrium is affected by heat and pressure in accordance with Le Chatelier's principle, and the solubility of a non-electrolyte is, in fact, an equilibrium constant. For substances which yield ions in solution, such as salts of formula MX, the equilibrium is of the form

$$\mathrm{MX\ (solid)} \rightleftharpoons \mathrm{M^+\ (in\ soln)} + \mathrm{X^-\ (in\ soln)}$$

and the equilibrium constant is the product of the activities (approximately, of the concentrations) of M^+ and X^- in solution, the activities of solids being taken arbitrarily as unity; this equilibrium constant is known as the *solubility product* of MX at the temperature chosen. For a salt of formula MX_2, the solubility product is $[M^+]\,[X^-]^2$, and so on. Since $[M^+]$ and $[X^-]$ are proportional to the amount of dissolved salt, we see that the relation between solubility and solubility product depends on the formula of the salt concerned.

One feature of discussions of solubility which calls for particular comment is the use of the term 'insoluble.' Most chemists tend to describe as 'insoluble' any substance which dissolves in a liquid to the extent of less than about 1 g in 1,000 g of solvent. Silver chloride and cupric sulphide, for example, are by this criterion insoluble in water. Their solubilities, 10^{-5} and 10^{-22} g-formula-weight per litre, and solubility products, 10^{-10} and 10^{-44} (g-ion/litre)^2, at 25°, however, are very different, and (as will be seen later) from the point of view of the energy change which would be involved in getting a g-formula-weight of solute into aqueous solution there is very much more difference between silver chloride and copper sulphide than between silver chloride and sodium chloride, the solubility of which is 0·62 g-formula-weight per litre at 25°.

We must now see why it is important to know something about such energy changes. It is well known that there are several forms of energy, such as mechanical, electrical, chemical and thermal energy. All forms of energy can be converted into heat, but the converse is not always true, and this has led to the division of the *total heat content* (H) at absolute temperature T of a system into two parts: that part which can be converted into other forms of energy without change of temperature is known as *free energy* (G), whilst the part which is not convertible ($H - G$) is defined as the product of the absolute temperature and a quantity called the *entropy* (S) of the system. Thus

$$H = G + TS$$

or, for a change taking place at constant temperature T,

$$\Delta H = \Delta G + T\Delta S$$

The quantity S may also be looked at in another way, as a measure of the degree of randomness of the system. This aspect may be illustrated by considering what happens if we mix equal quantities of hot and cold water: the resulting liquid all has the same temperature, and instead of there being molecules describable as belonging to one of two different categories, all are now mixed up—the randomness of the system has increased. At the same time, although no heat has been gained or lost, the possibility of using the system to obtain electrical energy by putting thermocouples in the water at different temperatures has disappeared. Gain in entropy is therefore accompanied by a corresponding loss in free energy if there is no change in the total heat content of the system. Just as every substance has a standard heat of formation, it has also a standard free energy of formation and a standard entropy, and from tables of such quantities (which may be determined independently by a variety of methods) it is possible to compute changes in them for different reactions.

The very existence of endothermic (heat-absorbing) processes which take place spontaneously (*e.g.* the dissolution of most substances in water) is a proof that it is not the change in heat content (ΔH) which determines how far a reaction goes, *i.e.* its equilibrium constant. This quantity is the free-energy change, which is therefore a quantity of the greatest importance throughout chemistry. It is not essential in obtaining some understanding of the significance of the concept of free energy in chemistry to master the numerical form of all the relationships involved, but one such relationship is of outstanding importance: if a reaction is carried out on a very small scale (say, one-millionth gram-formula quantities) in the presence of all the reactants and products at unit activity, and the free-energy change is multiplied (in this case by a million) to give the so-called standard free-energy change, ΔG°, the latter is related to the equilibrium constant for the reaction by an equation of the form

$$-\Delta G^\circ = \boldsymbol{R}T \ln K$$

where K is the equilibrium constant expressed in suitable units, $\boldsymbol{R}$ is the gas constant, T the absolute temperature, and ln denotes logarithm to base e, or $2{\cdot}3 \log_{10}$. Substitution of the values of $\boldsymbol{R}$ and T leads (for $T = 25°\text{C}$) to the equation

$$-\Delta G^\circ \text{ (in kcal)} = 1{\cdot}36 \log_{10} K$$

The special feature of this relationship which must be noted is that it is an exponential one. Since it is the logarithm of the equilibrium constant that is related to $-\Delta G^\circ$, a small change in the latter quantity makes a very large difference to how far a process goes; a change of 4 kcal in ΔG, in fact, alters K by a factor of a thousand. In the case of an ionic solid dissolving in water, the energies of interaction of the ions with one another in the solid and with water molecules in solution are both very large, and it is the small difference between these two large quantities (neither of which may be accurately known) which determines the magnitude of the solubility product (the equilibrium constant) and hence of the solubility: this is why the calculation of solubilities of salts from thermal data presents such a formidable task.

This competitive picture of the dissolution of salts may now be generalized to include all processes of solution. There will always be an increase in the entropy of the system when two constituents mix to form a solution, because of the increase in randomness, and in cases where there is no heat of solution this increase in entropy provides the driving force for the dissolution: such a case is illustrated by many pairs of organic liquids, which are freely soluble in one another without absorption or liberation of heat (if $\Delta H = 0$, $\Delta G = -T\Delta S$). Usually, however, it will be necessary to consider heat terms as well as entropy terms, and to what extent a solute A will dissolve in a solvent B will then be determined largely by the difference between the energy of interaction of A with B and the energies of interaction of A with A, and B with B. Looking at the problem in this way, we see that whether A dissolves in B depends just as much on the properties of the solvent as on the properties of the solute: hydrocarbons, for example, dissolve only very slightly in water, not because of strong attraction between hydrocarbon molecules in pure hydrocarbons but because of the hydrogen bonding between molecules in liquid water: the C–H bond is much less polar than the O–H bond, and hence bonds of the latter type interact with one another preferentially.

We shall now discuss some different types of solution to illustrate the relative importance of heat and entropy terms in determining the position of equilibrium.

SOLUTIONS IN GASES

Since the molecules of an ideal gas exert no force of attraction on one another, a gas as a solvent offers no resistance to dilution with another substance: there is always a positive entropy of mixing, and the position of equilibrium is determined largely by the amount of energy needed to separate the units present in the structure of the solute. If this is another gas, a negligible amount of energy is needed, and hence all gases are completely miscible. If it is a liquid or a solid, the latent heat of vaporization or sublimation must be absorbed in order to transform it into the vapour phase; this then mixes freely with the gas, which is considered to be the solvent. The influence of temperature is thus confined to its effect on the vapour pressure of the solute, and solubilities of liquids and solids in gases always increase with rise in temperature.

Occasionally there is evidence for specific interaction between a gaseous solvent and a solid solute; some metal oxides (*e.g.* BeO) are significantly soluble in compressed steam at high temperatures owing to hydroxide formation.

SOLUTIONS OF GASES IN LIQUIDS

Solubilities of gases in liquids are usually cited as absorption coefficients, as has been mentioned earlier; since, however, by Avogadro's law the number of moles of a gas is proportional to its volume at standard temperature and pressure, the absorption coefficient is evidently proportional to the concentration in moles per litre. One of the difficulties which arises in the interpretation of absorption coefficients (and, indeed, of many other solubility data) is that the analytical methods employed in their determination do not reveal the chemical form in which the solute has dissolved. It may reasonably be supposed that nitrogen and oxygen dissolve unchanged, for they are sparingly soluble in all solvents: but hydrogen chloride in water is largely converted into hydrated H_3O^+ and Cl^- ions: the fact that 2M ammonia solution has quite a strong odour, whereas 2M hydrochloric acid is odourless, indicates that for ammonia the degree of interaction with the solvent is smaller. All very soluble gases do, in fact, undergo chemical change to an appreciable extent in the solvents in which they are very soluble.

The solubility of a gas at a given temperature is proportional to the pressure (Henry's Law). If n_1 and n_2 are the numbers of moles of solvent and gas in the saturated solution at pressure p_2 of the gas,

$$n_2/n_1 = kp_2$$

If the gas is not very soluble, n_2 is much smaller than n_1, and n_1 is then nearly equal to $n_1 + n_2$, so that $n_2/(n_1 + n_2) = x_2 = kp_2$, where x_2 is the mole-fraction of solute in the saturated solution. Now if we think of the solvent as non-volatile, p_2 becomes the vapour pressure of the volatile solute present in mole-fraction x_2 in the solution. If Henry's Law applies over the whole concentration range from pure solvent to pure liquefied solute, then when x_2 is unity p_2 becomes p_2°, the vapour pressure of the pure solute, so that $k = 1/p_2^\circ$. Hence

$$x_2 = p_2/p_2^\circ \quad \text{or} \quad p_2 = x_2 p_2^\circ$$

This is, of course, Raoult's law for a liquid mixture. With its aid we can calculate the ideal solubility of any gas if the vapour pressure above its liquid is known at that temperature (*i.e.* if it is below its critical temperature). At 25°C, for example, the vapour pressure of pure liquid ethane is 42 atm; if $p_2 = 1$ atm, $x_2 = 1/42 = 0{\cdot}024$ mole-fraction. For gases above their critical points the hypothetical vapour pressure of the liquid can be estimated (from the Clausius–Clapeyron equation) on the assumption that the heat of vaporization remains constant: in this way it can be shown that the ideal solubility of nitrogen should be about 10^{-3} mole-fraction.

These calculated values, it should be noted, apply to *any* solvent so long as the solutions show ideal behaviour; the actual values for ethane and nitrogen in solvents such as hydrocarbons and carbon tetrachloride are about 0·018 and 6×10^{-4} mole-fractions, respectively, showing that there is some departure from ideality. It is, however, very striking that so simple a treatment leads to a result which is in error by less than a factor of two. When water is the solvent this is not so, for the intermolecular attraction in liquid water complicates the picture by making all gases which dissolve in molecular form much less soluble than they are calculated to be; the gain in entropy of mixing is offset by the work which has to be done against this intermolecular attraction in forcing molecules of solvent apart. Water is the outstanding example of a polar solvent with strong intermolecular attraction, but nitrobenzene, aniline and ethanol also show this behaviour to some extent; another manifestation of this in the case of ethanol is the fact that its boiling point is 100° higher than that of dimethyl ether, which has the same molecular weight.

The inverse dependence of x_2 on p_2° at a particular temperature also explains two other features of the solubility of gases. Since the pressure above the liquid is less for gases with relatively high boiling points, gases such as butane and carbon dioxide are much more soluble in all solvents than are hydrogen, oxygen, nitrogen and carbon monoxide. Furthermore, since for any gas p_2° increases with increase in temperature, the solubilities of all gases decrease with rise in temperature.

The latter conclusion may also be reached by Le Chatelier's principle: dissolution of a gas in a liquid may be considered as involving first the condensation of the gas, followed by mixing of the two liquids; since the condensation stage is accompanied by liberation of heat, lowering the temperature will cause more gas to dissolve.

SOLUTIONS OF LIQUIDS IN LIQUIDS

Mixtures of two volatile liquids which are miscible in all proportions are in many ways like solutions of gases in liquids. If in the preceding solution p_2° is less than 1 atm at 25° and the phase designated the solvent has an appreciable vapour pressure, we have a typical binary liquid system. Each liquid in such a mixture exerts a vapour pressure equal to its mole-fraction times its vapour pressure in a pure state at the same temperature (Raoult's Law); solutions for which this law holds are called ideal solutions, and typical examples are usually mixtures of very similar substances such as ethyl bromide and ethyl iodide, or benzene and toluene. It would be rather surprising if there were many pairs of liquids which obeyed Raoult's law exactly, since the existence of a substance in the liquid phase at all is a proof of the presence of quite strong intermolecular attractions which can be overcome only by supplying the heat of vaporization. When an ideal solution is formed from two liquids there is no change in heat content; the driving force towards mixing is provided by the increase in entropy.

There are, of course, many pairs of liquids which are miscible in all proportions to yield mixtures which show deviations from Raoult's law, *e.g.* diethyl ether and acetone, heptane and ethanol, ethanol and water, perchloric acid and water. These deviations arise from the differences in properties of the constituents of the pairs, and in some cases there are appreciable heats of mixing. The nature of these deviations from Raoult's law is, however, of minor interest in connection with solubility, and will not be discussed further here.

When two liquids are less similar than the members of the pairs cited above, partial miscibility usually occurs; if a little phenol, aniline or ether, for example, is added to water, it dissolves, but further additions soon result in the formation of two layers, one a saturated solution of the organic compound in water, and the other a saturated solution of water in the organic compound. Similar behaviour also results with aniline and n-hexane, or methanol and carbon disulphide. Greater difference in nature (*e.g.* water and carbon disulphide, ethanol and mercury) results in immiscibility. The miscibility of liquids is often discussed in terms of their *internal pressures*, which may be regarded as measures of the dependence of internal energy on volume, *i.e.* of the strength of the cohesive forces. These may be estimated roughly by several methods, typical values at ordinary temperature being: hexane, 2,000; carbon tetrachloride, 3,500; phenol, 5,000; water, 16,000 atm. Increasing difference in internal pressures leads to decreasing solubility; increasing temperature overcomes the cohesive forces, and many pairs of partially miscible liquids become completely miscible at higher temperatures.

The observant reader will have noticed that no question of absorption or liberation of a heat of fusion or vaporization arises in the dissolution of one liquid in another; the overall heat of solution is therefore nearly always small and arises from different degrees of non-ideality in the liquids concerned. Clearly, entropy considerations play an important part: but it cannot be said that at the present time there is any simple theory which deals satisfactorily with all of the great variety of behaviour found in liquid–liquid systems.

SOLUTIONS OF SOLIDS IN LIQUIDS

Three types of solid will be considered in the following discussion: those having molecular, macromolecular and essentially ionic structures.

In molecular solids the shortest distances between atoms in different molecules are about twice the interatomic distances within molecules; the intermolecular bonding is weak, as is shown by the low heats of sublimation. Among substances which crystallize with molecular structures at the ordinary temperature are iodine, mercuric chloride and nearly all organic compounds.

Macromolecular structures, such as those of diamond, silica and red phosphorus, contain no discrete molecules: strong covalent bonds extend through the structure in two or more directions, and it is only with great difficulty that the lattice can be broken up.

Ionic solids contain symmetrical arrangements of charged ions held together by electrostatic bonding, the energy of the lattice relative to isolated ions at infinity being proportional to $1/(r_+ + r_-)$, where $(r_+ + r_-)$ is the sum of the ionic radii, *i.e.* the interionic distance. Although salts have very high heats of fusion and vaporization, the ions are strongly attracted by polar molecules (especially water) and solvation energies of ions are sometimes greater than lattice energies of salts containing them.

If a molecular solid is melted (thereby absorbing the latent heat of fusion), the resulting liquid may form an ideal solution with a solvent; when this is so, the heat of fusion is equal to the heat of solution, and it can be shown by a rather lengthy thermodynamic argument (which will not be reproduced here) that the ideal solubility under constant pressure is given by

$$\ln x = -\frac{L_f}{\boldsymbol{R}}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

where T is the temperature at which the mole-fraction of the solute in the solution is x, L_f is the molar heat of fusion of the solid, and T_0 is its melting point. This equation may, for example, be used to calculate the ideal solubility of naphthalene in any solvent as 0·31 mole-fraction at 25°C. The solubilities in benzene, toluene, chlorobenzene and chloroform (all of which are non-polar liquids having internal pressures similar to that of liquid naphthalene) are all close to this value; those in aniline and acetone agree less well: in water, naphthalene is very sparingly soluble, since the strong attraction of water molecules for one another (made manifest in the high boiling point, entropy of vaporization, and internal pressure of water) serves to exclude molecules of the non-polar solute. It is, in fact, the abnormal character of water which is responsible for the low solubility of most organic compounds in it; the organic compounds which are soluble in water all contain groups such as hydroxyl, carboxyl or sulphonyl, which can interact with water molecules as strongly as the latter interact with one another. Typical compounds in these classes are low-molecular-weight alcohols and acids, polyhydric alcohols such as sugars, and soaps.

For a macromolecular solid which is imagined to form an ideal molecular solution, similar considerations should apply; in this case, however, the latent heat of fusion is extremely high and hence the solubility in all solvents is extremely low.

For ionic solids the position of equilibrium is determined mainly by the balance of lattice energies and solvation energies. In a more refined treatment the latter would be split into heat and $T \times$ (entropy of solvation) terms, but for present purposes a discussion based on lattice energy and hydration heats will suffice; as has been stated earlier, both are very large quantities, but it is the small difference between them which determines solubilities. In the case of sodium chloride, for example, it requires absorption of 184 kcal/g-formula-weight to separate the solid into ions at infinity; since the heat of solution of sodium chloride in water is nearly zero (hence the independence of solubility on temperature) the sum of the hydration heats of Na^+ and Cl^- must also be 184 kcal. Most other salts absorb a few kcal of heat on dissolution in water, and hence are more soluble in hot than in cold water; the increase in solubility is, however, usually relatively small. In principle the hydration energy of an ion of radius r and charge z in a solvent of dielectric constant ϵ is given by the expression

$$\frac{z^2e^2}{2r}\left(1 - \frac{1}{\epsilon}\right)$$

but the radius of an isolated ion in solution is not necessarily the same as that of the same ion in a crystal, and ϵ need not be the same near an ion as it is in the pure solvent; in practice, therefore, empirical methods play a large part in obtaining values for solvation energies. The importance of the $(1-1/\epsilon)$ term, however, is very great, for it means that only in solvents of high dielectric constant will the sum of two solvation energies approach the lattice energy of the solid. Hence salts, if they dissolve at all, will normally do so only in media of high ϵ, such as water, ammonia, nitromethane and dimethylformamide. The few salts that dissolve in organic solvents of low dielectric constant (*e.g.* ether) nearly always contain very large ions and have very low lattice energies; tetrabutylammonium picrate is an example of such a compound.

The fact that the lattice energy of an ionic solid depends inversely on $r_+ + r_-$ taken together, whilst the sum of the solvation energies is proportional to $1/r_+ + 1/r_-$ taken separately, has other instructive consequences. For a set of compounds having the same structure and $r_- \gg r_+$ the lattice energies change little with increasing r_+; $1/r_-$ is constant and very small, whilst $1/r_+$ decreases rapidly with increase in r_+. Hence solubilities decrease as r_+ increases; this is what happens among, for example, the alkali-metal chloroplatinates or cobaltinitrites or the alkaline-earth metal sulphates in water. Insolubility in water thus need not denote covalent character; there is, for example, not the slightest evidence to suggest that the bonding between the metal and the anion in calcium fluoride, barium sulphate or potassium chloroplatinate is not ionic.

Silver ion has almost the same radius as sodium ion, and silver fluoride is freely soluble in water. Silver chloride, however, is very sparingly soluble, and it is instructive to compare the pairs NaF and NaCl, and AgF and AgCl. The observed lattice energies of these four compounds (all of which have the NaCl structure) are 216, 184, 228 and 216 kcal/g-formula-weight respectively. Despite the difference in size between F^- and Cl^-, we notice that the difference in lattice energy is only 12 kcal for the silver salts; for the sodium salts it has the much larger value of 32 kcal. We therefore infer that there is about 20 kcal of non-electrostatic bonding stabilizing the solid in the case of silver chloride; this term has no counterpart in the hydration energies of Ag^+ and Cl^- in water, which are the same as in solutions of silver fluoride and sodium chloride, and it is therefore the main factor underlying the striking difference in solubility in water between silver fluoride and silver chloride.

The foregoing account of the solubility of salts has been based on an electrostatic model for the solvated ion in solution, the charge on the ion interacting with the uneven charge distribution in the water or other solvent molecule. There is sometimes, however, very strong evidence that the solvation process is not a simple electrostatic one. Thus when a paramagnetic Co^{3+} ion is hydrated, it becomes diamagnetic, showing that an electronic rearrangement has taken place. When $Cr(H_2O)_6^{3+}$ ions from chrome alum dissolve in ^{18}O-labelled water, it is found that no exchange with water from the alum takes place during several hours; evidently the water attached to the cation is not free to exchange, a fact which again suggests covalent bonding. Finally, the highly specific interaction between salts of a few metals and organic liquids, *e.g.* the solubility of silver fluoroborate (which has the same structure as potassium fluoroborate) in benzene and toluene, indicates covalent interaction of a rather special kind, in this case between the aromatic compound and the silver ion. In all these cases, however, it should be remembered that the position of equilibrium is determined by the difference between the lattice energy of the solid and the *magnitude* (not the *nature*) of the interaction between ions and solvent: it is the magnitude of the free-energy change which determines how far the process of dissolution goes.

SOLUTIONS IN SOLIDS

The characteristic feature of a solid is that it contains atoms, molecules or ions occupying particular positions in a rigid structure. When the solute can be accommodated in the solvent lattice without appreciable change, the formation of a solid solution takes place readily: examples are provided by *p*-dichlorobenzene and *p*-dibromobenzene, potassium chloroplatinate and potassium bromoplatinate, magnesium oxide, MgO, and lithium ferric oxide, $LiFeO_2$ (Mg^{2+}, Li^+ and Fe^{3+} are the same size, and the average charge on Li^+ and Fe^{3+} is the same as on Mg^{2+}), and silver and gold. In such cases, there is a negligible change in heat content when a solid solution is formed. Gases and liquids, on the other hand, are seldom very soluble in solids: the fact that they *are* gases and liquids implies a simple molecular structure in their solid phases, and solubility is then to be expected only in elements or compounds crystallizing with similar simple molecular structures. For a gas or a liquid to dissolve in a solid requires work to be done in forcing apart the units in the solid structure and, since the interatomic, intermolecular or interionic forces in solids are relatively strong, this energy factor militates against solubility. Gases usually interact with solids only to the extent of forming a monolayer held by surface forces and a weakly held layer, only a few molecules thick, on top of this. Where the solubility is appreciable, as in the case of hydrogen in palladium and other metals, strong chemical bonding must be involved to compensate not only for the work done in expanding the metal lattice, but also for the energy needed to break the strong bonds (103 kcal/mole) in hydrogen, which is present in the solid phase as single atomic units.

CONCLUSION

The positions of all equilibria are determined by thermodynamic factors. When solute and solvent are in the same physical state, the increase in entropy on mixing ensures solubility so long as (i) in the case of liquids, they do not differ too widely in their properties and internal pressures; (ii) in the case of solids, they have the same structure and, if ionic, contain ions of similar sizes. For other cases, heats of vaporization or fusion are involved as well as entropies of mixing. In all cases, however, the key to the interpretation of solubility lies in the evaluation of the free-energy change which accompanies the process of dissolution.

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Nos lecteurs trouveront ci-dessous l'article de notre collègue Fairbank sur les acides et les bases selon la conception de Brönsted ; cet article développe une intervention orale faite lors de notre réunion du 25 avril. S'appuyant sur son expérience des classes secondaires, notre collègue préconise l'introduction des idées de Brönsted dès un niveau élémentaire. Dans un article que j'avais précédemment publié dans notre bulletin n° 468 (page 337 et suivantes), j'avais émis quelques réserves concernant la communication des conceptions de Brönsted aux élèves des classes du second cycle ; je demandais alors aux professeurs plus compétents que moi-même à ce sujet de nous donner leur avis. Voilà qui est fait et fort brilamment ; j'avoue que j'ai été parfaitement convaincu par les arguments de Fairbank et je dois avouer que j'en suis très heureux.

P. MARCK.

Acidité et basicité au sens de Brönsted dans l'enseignement du second cycle

Les conceptions de Brönsted en matière d'acidité et de basicité sont de plus en plus utilisées de nos jours, dans les laboratoires de recherche, dans l'enseignement supérieur, dans les classes préparatoires aux grandes écoles.

A la suite de la réunion du Club Pédagogique de l'U.D.P. au lycée Louis-le-Grand à Paris, le 25 avril 1963, et de différents articles du bulletin (1), se pose alors la question de la possibilité et surtout de l'utilité d'un usage de ces notions dans les classes du Second Cycle. C'est ce problème que nous examinerons ici.

Depuis l'introduction dans les programmes de 1re, en 1957, de la théorie des ions, les définitions suivantes, appelées couramment définitions d'Arrhénius, sont généralement adoptées pour les acides et les bases :

Un acide est un corps capable de fournir des ions H^+.

Une base est un corps capable de fournir des ions OH^-. De telles définitions entrainent avec elles tous les avantages des exposés fondés sur les conceptions ioniques : les propriétés d'un corps (électrolyte) sont celles de ses ions. Mais précisément, un cours sur les acides (ions H^+), ou sur les bases (ions OH^-), ne sera pas *dans sa forme* très différent d'un cours sur les sels de zinc (ions Zn^{++}) par exemple, ou sur les sulfates (ions SO_4^{--}). Or il y a dans les notions d'acide et de base quelque chose de plus, et que les définitions précédentes ne mettent pas en évidence : leur caractère antagoniste et complémentaire, leur caractère conjugué, dû à leur réaction fondamentale de neutralisation réciproque.

La première idée, essentiellement pratique et expérimentale que les élèves se font des acides et des bases, est une idée unitaire. En 2^{me}, lors du cours sur l'oxygène, et en travaux pratiques, c'est par leur action sur les indicateurs colorés qu'acides et bases sont provisoirement définis ; et la réversibilité de cette action impose irrésistiblement l'idée que l'un est le contraire de l'autre.

Dans l'échelle des *p*H, on évalue aussi bien l'acidité que la basicité, comme avec une seule échelle de température on évalue le « chaud » et le « froid ».

La notion d'acidité et de basicité est donc bien une notion unitaire ; c'est la première notion intuitive que s'en font les élèves ; c'est à quoi ont abouti rationnellement les conceptions théoriques ; c'était déjà l'idée que s'en faisaient les chimistes du 18^e siècle, définissant les acides « *des corps raides longs, pointus, tranchants, et tout à fait propres à s'insinuer dans des espèces de gaines ou de corps poreux et spongieux qu'on nomme alkalis* » et inversement les bases ou alkalis comme « *des corps poreux et spongieux dans lesquels comme dans autant d'espèces de gaines vont se loger des corps raides longs, pointus et tranchants qu'on nomme acides* ». Même la comparaison pédagogique n'est pas oubliée : « *Pour donner une idée sensible des uns et des autres, on a coutume de comparer un acide fermé dans son alkali à une épée que l'on a fait entrer dans son fourreau* ». (2)

C'est dans ce courant intuitif et naturel (3), aussi traditionnel que moderne, que nous replace la théorie de Brönsted en énonçant simplement :

Un acide est un corps capable de fournir des ions H^+.

Une base est un corps capable de fixer des ions H^+.

On a là toute la théorie de Brönsted, il n'y a rien de plus... sinon à utiliser ces définitions.

I. *Acides classiques.*

Tous les acides au sens traditionnel du terme le seront au sens de Brönsted, ce qui est assez naturel puisque la définition de Brönsted coïncide avec la définition d'Arrhénius.

II. *Bases classiques.*

Toutes les bases classiques le seront encore au sens de Brönsted :

Les hydroxydes solubles tels que la soude, parce que libérant des ions OH^- qui fixent les ions H^+ dans la réaction :

$$(1) \qquad OH^- + H^+ \rightarrow H_2O$$

Nuance : au sens classique, c'est NaOH la base ; pour Brönsted, c'est l'ion OH^- lui-même. Mais en définitive, qu'est-ce que la base NaOH ? C'est un ensemble d'ions Na^+ et OH^-, *et qui n'est appelé base qu'à cause de ces ions* OH^-. Alors, ne peut-on continuer à appeler base cet ensemble d'ions, puisqu'aussi bien un ion ne peut être pris isolément ? Ce n'est qu'une très légère extension de sens.

Seront encore des bases les hydroxydes basiques insolubles comme $Cu(OH)_2$ par exemple. Dès l'instant qu'on écrira leur réaction avec les acides sous la forme :

$$(2) \qquad Cu(OH)_2 + 2\ H^+ \rightarrow Cu^{++} + 2\ H_2O$$

ce caractère deviendra évident, plus évident même qu'avec la définition d'Arrhénius où il fallait parler d'abord d'une progressive dissociation en ions OH^-, sous l'action de l'eau, puis de l'acide. On pourra cependant dire que l'ion H^+ de l'acide a en quelque sorte « arraché » un ion OH^- à $Cu(OH)_2$, et toutes ces bases au sens traditionnel pourront être considérées comme formant une première et importante famille, celle des hydroxydes basiques ; *c'est dire que la définition des bases d'Arrhénius pourra continuer à être employée, mais on la posera non comme une définition, mais comme une simple conséquence de la définition de Brönsted.*

III. *Oxydes basiques.*

Reconnaissant le comportement basique de la plupart des oxydes métalliques, la nomenclature classique leur donnait déjà le nom d'oxyde basique. Du point de vue de Brönsted, ce seront effectivement des bases, une seconde famille de base. Un oxyde tel que CuO, ne fixe-t-il pas les ions H^+ dans sa réaction sur les acides :

(3) $CuO + 2\ H^+ \rightarrow Cu^{++} + H_2O$

L'hydratation d'un oxyde basique soluble, comme Na_2O, correspond aussi à un tel processus, mais alors c'est l'eau qui joue le rôle d'acide :

(4) $Na_2O + 2\ H^+ \rightarrow 2\ Na^+ + H_2O$

(5) $2\ H_2O \rightarrow 2\ H^+ + 2\ OH^-$

et en additionnant, on retrouve la réaction classique :

(6) $Na_2O + H_2O \rightarrow 2\ Na^+ + 2\ OH^-$

IV. *Action des bases sur les sels.*

Sous ce titre général, on n'étudiait en théorie classique que la seule action des hydroxydes basiques *solubles* (soude, potasse). De fait, il s'agissait de propriété de l'ion OH^- *libre* (en quantité suffisante), et c'est pourquoi les hydroxydes insolubles sont sans action. On fera la même chose en théorie de Brönsted, mais ce sera plus net : C'est l'action de *la base particulière* OH^- ,et non des bases en générale qu'on étudiera.

V. *Le cas de l'ammoniac.*

Il était au fond assez délicat à traiter. L'action de l'acide chlorhydrique sur l'ammoniac, en phase gazeuse (4) s'écrit :

(7) $HCl + NH_3 \rightarrow NH_4Cl$

Ce n'était pas l'action d'un acide sur une base.

Mais en solution aqueuse tout changeait :

admettant d'abord, (8) $NH_3 + H_2O \rightarrow NH_4OH$

on écrivait : (9) $HCl + NH_4OH \rightarrow NH_4Cl + H_2O$

et cette réaction (9) *était bien l'action d'un acide sur une base.* Or, en additionnant (8) et (9), on retrouvait (7) ! Par ailleurs, si la réaction (8) apparaissait justifiée au point de vue expérimental par la nécessité de donner à l'ammoniaque une formule d'hydroxyde basique, les causes *théoriques* d'une telle réaction restaient mystérieuses.

En théorie de Brönsted, tout s'éclaircit : La réaction (7) est considérée comme l'action d'un acide sur une base. En effet, l'acide HCl a bien fourni un ion H^+, et la base NH_3 l'a fixé, devenant l'ion NH_4^+, qui reste uni par liaison ionique à l'ion Cl^-. En solution aqueuse, du fait de la dissociation ionique de HCl et de NH_4Cl, on écrira simplement :

(10) $NH_3 + H^+ \rightarrow NH^+_4$

mais l'identité des réactions (7) et (10) n'en sera pas moins évidente.

Quant à l'action de la solution aqueuse d'ammoniac (l'ammoniaque) sur les sels métalliques, elle ne soulèvera aucune difficulté, bien au contraire : On dira que l'ammoniac NH_3, de par son caractère basique peut « arracher » des ions H^+ à l'eau pour former l'ion NH^+_4, tout comme elle l'avait fait à la molécule HCl en phase gazeuse dans la réaction (7), et cette analogie est d'autant plus exacte que les liaisons dans HCl gazeux et dans H_2O sont on le sait, partiellement covalentes, partiellement ioniques. On écrira donc finalement l'équation :

$$(11) \qquad NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

et l'apparition des ions OH^- justifiera l'action de l'ammoniaque sur les sels. Dans la mesure où les élèves s'étonneront de la réaction (11), on pourra plus facilement leur expliquer qu'elle n'est que partielle, que progressive, d'où le caractère de « base faible » de l'ammoniac NH_3 ; tout ceci sans avoir besoin de soulever à propos de la réaction (11) qui est réversible, le problème délicat des déplacements d'équilibre. On pourra aussi « laisser remarquer » que l'eau, dans une telle réaction joue le rôle d'acide. Finalement, on voit qu'on n'aura guère à parler de molécule NH_4OH. Il est probable que les solutions ammoniacales correspondent à un équilibre complexe d'ions (NH_4^+, H^+, OH^-) et de molécules (NH_3, NH_4OH, H_2O). On ne peut parler de tout à la fois. La théorie classique était centrée sur NH_4OH. Un exposé à la Brönsted permet de s'en passer, et est centré sur la seule molécule NH_3. C'est une simplification.

V. *Hydrolyse des sels* (5).

Il est difficile de passer sous silence l'acidité ou la basicité aux indicateurs colorés des solutions salines tant le phénomène est courant, banal, frappant : La solution — bleue — de sulfate ou de nitrate de cuivre ($pH = 4$) rougit un papier tournesol bleu. La solution de carbonate (neutre !) de sodium ($pH = 11,5$) rougit magnifiquement la phtaléine du phénol. Les solutions de chlorure, de sulfate, de nitrate ferrique sont plus acides que l'acide acétique ($pH = 2$). Quant au carbonate *acide* (hydrogénocarbonate) de sodium, on sait que sa solution à « scandaleusement » un léger caractère basique ($pH = 8,5$), rosissant faiblement la phtaléine. Dans quel abîme de perplexité ne plongeait-on pas l'esprit des élèves ! Surtout avec les explications réduites qu'on pouvait leur donner, distinguant subtilement entre sel acide, et sel neutre à réaction acide avec certains indicateurs colorés, sel basique, et sel neutre à réaction basique avec certains indicateurs colorés, *ce qui impliquait d'ailleurs la non spécificité des indicateurs colorés pour les acides et les bases.*

A) *Sels à réaction basique.*

Soit un acide HA susceptible de se dissocier en ions H^+ et A^-. Si l'acide est fort, il se dissocie totalement, c'est-à-dire qu'il cède ses ions H^+ facilement. Si l'acide est faible, il ne se dissocie que faiblement, il ne cède ses ions H^+ que difficilement. *Réciproquement, si nous considérons les anions A^-, ils auront tendance à se combiner avec les ions H^+ (propriété basique) dans le cas d'un acide faible, alors que cette tendance sera inexistante dans le cas d'un acide fort (aucune propriété basique).*

Si nous prenons donc des anions A^- d'acide faible séparés de leurs ions H^+, en utilisant par exemple le sel de sodium NaA, à l'adjonction des ions H^+ d'un acide, c'est la réaction :

$$(12) \qquad A^- + H^+ \rightarrow HA$$

qui se fera.

Exemple : Une solution d'hélianthine rosie (6) par un acide est ramenée au jaune par une solution d'acétate, de borate, ou de carbonate de sodium.

Si les ions A^- sont en la seule présence des molécules d'eau, leur caractère basique pourra être assez fort pour qu'ils arrachent des ions H^+ aux molécules d'eau selon :

$$(13) \qquad A^- + H_2O \rightarrow HA + OH^-$$

(c'est la classique réaction d'hydrolyse, mais intégrée dans un schéma plus général).

Exemples : Une solution de carbonate de sodium Na_2CO_3 (pH = 11,5) rougit énergiquement la phtaléine, une solution de borate de sodium (pH = 10) la rougit aussi, mais, un peu moins bien, une solution d'acétate de sodium (pH = 7,5) est sans action.

Dans le cas des ions acétate et borate, on pourra se borner à utiliser le symbole A^- sans préciser ; mais, pour l'ion carbonate CO_3^{--}, il faudra expliciter les réactions (12) et (13). C'est la 2^e^ acidité de l'acide carbonique, extrêmement faible, qui entraine pour l'ion carbonate CO_3^{--} un caractère basique relativement fort. On écrira donc :

$$(12\ \text{bis}) \qquad CO_3^{--} + H^+ \rightarrow HCO_3^-$$

$$(13\ \text{bis}) \qquad CO_3^{--} + H_2O \rightarrow HCO_3^- + OH^-$$

Notons que la réaction (12 bis) explique *naturellement* la redissolution de $CaCO_3$ par un excès de CO_2 ou par un acide en solution très diluée (sans dégagement de CO_2), alors que dans les exposés traditionnels, c'était une exception à la règle de Berthollet :

$$(14) \qquad CaCO_3 + H^+ \rightarrow HCO_3^- + Ca^{++}$$

C'est simplement l'action de l'ion H^+ sur la base CO_3^{--} ; l'apparition d'ions Ca^{++} vient seulement du fait que l'ion CO_3^{--} n'est pas libre, mais « prisonnier » dans le réseau cristallin du carbonate de calcium.

B) *Sels à réaction acide.*

Soit par exemple, du sulfate ferrique : Sa solution rougit l'hélianthine. Il faut insister sur le rôle de l'eau : Mettons dans un tube à essais 1 centimètre d'eau distillée et 2 gouttes d'hélianthine : solution jaune. Jetons-y une pincée de sulfate ferrique, la solution reste d'abord jaune, puis si on agite légèrement le tube, la dissolution s'opère, et l'hélianthine vire au rose. Du fait de l'insolubilité de l'hydroxyde ferrique $Fe(OH)_3$, l'ion Fe^{+++} « attire » d'une manière générale les ions OH^-, et est capable de les « extraire » des molécules d'eau qui l'entourent :

$$(15) \qquad Fe^{+++} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+$$

On sent très bien ici une notion d'acide qui serait « symétrique » en quelque sorte de celle de Brönsted : Un acide est un corps avide d'ions OH^-. Mais une telle définition finalement ne ferait que compliquer les choses si elle devait s'ajouter à la définition de Brönsted. Pour conserver ce caractère unitaire qui est le principal avantage des conceptions Bröstediennes, il suffit de considérer comme acide, *l'ensemble de l'ion Fe^{+++} et des molécules d'eau voisines*. Ce point de vue est d'autant plus exact que la plupart des ions en solution aqueuse sont hydratés, et que si beaucoup de propriétés peuvent s'expliquer sans tenir compte d'un tel phénomène, il ne saurait être question de tout interpréter en le négligeant systématiquement.

Pour simplifier, on utilisera l'équation (15), identique dans sa forme à la classique réaction d'hydrolyse, mais en adoptant le point de vue de Brönsted, c'est-à-dire en considérant comme acide l'ion ferrique hydraté. Bref, on négligera le degré exact d'hydratation, *mais non le phénomène lui-même* (7).

Le cas des sulfate, nitrate, et chlorure d'ammonium doit être étudié à part. La solution de chlorure d'ammonium par exemple, est faiblement acide ($pH = 5$) ; tout comme la solution aqueuse de gaz carbonique, elle décolore la phtaléine rougie par un minimum de base, ou fait virer au rouge vineux le traditionnel tournesol. Or si par de telles réactions nous prétendons montrer aux élèves le caractère acide de la solution carbonique, nous nous l'interdisons, *nous leur interdisons* dans le cas du chlorure d'ammonium ! Certes, en évaporant la solution contenant soude et gaz carbonique, on peut obtenir un nouveau sel, disons le carbonate de sodium si les proportions sont convenables, et dont on considère l'obtention comme le témoignage d'une réaction acide + base. Mais, un mélange de chlorure d'ammonium et de soude, en solution aqueuse, donne aussi par évaporation un nouveau sel, le chlorure de sodium !

La théorie de Brönsted considère simplement que l'ion NH_4^+ est dissocié (partiellement) dans la solution aqueuse selon :

(16) $$NH_4^+ \rightarrow NH_3 + H^+$$

bref, que c'est un acide (faible) ; et tout est expliqué : Le pH acide de la solution, et la véritable neutralisation acide base qu'est l'action de la soude (l'ion OH^-) :

(17) $$NH_4^+ + OH^- \rightarrow NH_3 + H_3O$$

de la chaux éteinte :

(18) $$NH_4^+ + Ca(OH)_2 \rightarrow NH_3 + 2\ H_2O + Ca^{++}$$

ou de la chaux vive :

(19) $$2\ NH_4^+ + CaO \rightarrow NH_3 + H_2O + Ca^{++}$$

On pourra remarquer que la réaction (16) est l'inverse de la réaction (10), première notion de réaction réversible. Il peut sembler délicat d'avoir à considérer ces deux réactions sans faire appel *explicitement* à la notion d'équilibre. En fait, il est assez facile de faire comprendre qu'en présence d'un acide, c'est (10) qui se produira, et en présence d'une base c'est (16) qui aura lieu.

C) *Sels à réaction neutre.*

Les sels d'acide fort et de base forte, comme NaCl par exemple, sont neutres aux indicateurs colorés. La théorie de Brönsted interprète ce fait de la façon suivante : L'acide chlorhydrique HCl est fort, c'est-à-dire complètement dissocié. Donc, l'anion Cl^- n'a aucune tendance à se recombiner avec les ions H^+, *bref n'a pas de propriétés basiques*. De même, la soude NaOH est une base forte, donc, le cation Na^+ n'a aucune tendance à se recombiner avec les ions OH^-, et notamment n'a aucune tendance à arracher des ions OH^- aux molécules d'eau qui l'environnent pour finalement libérer des ions H^+, *bref n'a aucune propriété acide*.

Comme on l'a vu en A) plus un acide est fort, plus les propriétés basiques de son anion sont faibles. D'une manière générale, les anions d'acides forts comme Cl^-, SO_4^{--}, NO_3^- auront des propriétés basiques infiniment faibles. De même, les cations de bases fortes n'auront en présence d'eau que des propriétés acides négligeables. En somme, c'est le cas limite.

D) *Sels d'acides faibles et de bases faibles.*

On interprétera leurs propriétés à la lumière des exemples précédents. Leurs solutions seront des mélanges d'acide (le cation hydraté), et de base (l'anion). Le plus fort imposera son caractère au pH de la solution. Ainsi, le carbonate d'ammonium aura un pH basique, parce que la force de la base (l'ion CO_3^{--}) est supérieur à la force de l'acide (l'ion NH_4^+) comme le montrent immédiatement les valeurs des constantes d'équilibre correspondantes.

Pour conclure cette étude de l'hydrolyse (je préfère dire : du pH des solutions salines), je voudrais insister sur le fait qu'elle ne représente qu'un essai d'exposé élémentaire de « l'hydrolyse » selon les conceptions de Brönsted, et non un cours à faire nécessairement, et dans son intégralité, en 2^me^ et en 1^re^. Je n'ai même pas supposé une étude systématique préalable des équilibres (je crois qu'on peut s'en passer), d'où l'absence de symbole $\rightleftarrows$ dans les réactions réversibles. Au maître d'adapter à sa guise son exposé relativement à ce dernier point selon le niveau des élèves.

VI. *Les amphotères, et le cas du « bicarbonate » de sodium.*

Les amphotères traditionnels rentrent naturellement dans le cadre de la théorie de Brönsted. L'hydroxyde de zinc par exemple, est acide selon :

$$Zn(OH)_2 \rightleftarrows ZnO_2^{--} + 2\ H^+ \qquad (20)$$

ou basique selon :

$$Zn(OH)_2 + 2\ H^+ \rightarrow Zn^{++} + 2\ H_2O \qquad (21)$$

La réaction (20) est infime dans l'eau pure, mais presque totale en présence d'une base forte telle que OH^-, capable « d'arracher » à l'hydroxyde ses ions H^+ :

$$Zn(OH)_2 + 2\ OH^- \rightarrow ZnO_2^{--} + 2\ H_2O \qquad (22)$$

Mais la théorie de Brönsted introduit une autre famille d'amphotère ; nous avons vu que l'hydrogénocarbonate de sodium (ou bicarbonate, ou carbonate « acide ») avait un pH légèrement basique (pH = 8,5 : la solution rosit faiblement la phtaléine). Il y a là, dans la théorie classique, une antinomie conceptuelle assez choquante (carbonate acide, pH basique), et que la théorie de l'hydrolyse ne supprime pas vraiment.

Or, que dit le « bon sens », indépendamment de toute théorie ? Que l'hydrogénocarbonate de sodium est encore acide.. puisqu'on peut le neutraliser plus avant, jusqu'au stade carbonate ; et, cependant, qu'il est basique... d'après sa réaction à la phtaléine. *Or, c'est exactement ce que reconnaît la théorie de Brönsted,* en le considérant comme *un amphotère.*

L'ion hydrogénocarbonate est en effet acide, très faible :

(23) $HCO_3^- \rightleftarrows CO_3^{--} + H^+$

soit en présence d'ions OH^- en excès :

(24) $HCO_3^- + OH^- \rightarrow CO_3^{--} + H_2O$

et il est aussi basique, d'après :

(25) $HCO_3^- + H^+ \rightleftarrows H_2CO_3$

d'où en présence d'eau pure jouant le rôle d'acide :

(26) $HCO_3^- + H_2O \rightleftarrows H_2CO_3 + OH^-$

Ainsi la contradiction se trouve élégamment résolue, dans le cadre de la théorie de Brönsted, par la diacidité faible de l'acide carbonique.

Les mêmes explications valent pour les pH basiques des solutions aqueuses des sulfures de sodium et de potassium, dûs à la base S^{--}.

Elles ne valent pas pour les solutions de sulfate de sodium ou de potassium, car les deux acidités de l'acide sulfurique sont toutes deux relativement fortes, c'est-à-dire que les ions sulfate SO_4^{--} et hydrogénosulfate n'ont qu'un caractère basique négligeable.

VII. *Les réactions ioniques en chimie organique.*

Toutes les notions précédentes peuvent être utilisées en chimie organique, non seulement pour des corps tels que les acides organiques, les phénols simples ou substitués, les bases aminées, mais encore pour ceux à qui la chimie attribue maintenant un mécanisme ionique pour certaines de leurs réactions.

Le mécanisme de l'action de l'alcool éthylique sur le sodium par exemple peut être analysé comme suit :

(27) $C_2H_5OH \rightarrow C_2H_5O^- + H^+$

(28) $Na \rightarrow Na^+ + e^-$

(29) $H^+ + e^- \rightarrow \frac{1}{2} H_2 \nearrow$

(30) $C_2H_5O^- + Na^+ \rightarrow C_2H_5ONa$

Dans la réaction (27) l'alcool a joué le rôle d'un acide, acide très faible ($pK_a \simeq 15{,}9$), plus faible même que l'eau ($pK_a = 15{,}74$).

La décomposition de l'alcoolate par l'eau est alors une véritable hydrolyse qu'on peut analyser ainsi :

(31) $C_2H_5ONa \rightarrow C_2H_5O^- + Na^+$

(32) $C_2H_5O^- + H_2O \rightarrow C_2H_5OH + OH^-$

Cette hydrolyse est ici totale, l'acidité très faible de l'alcool entrainant une basicité très forte pour l'ion alcoolate $C_2H_5O^-$, plus forte que celle de l'ion OH^-. La non-réaction de l'alcool sur la soude se trouve expliquée du même coup.

Considérons maintenant la réaction de l'acétylène sur le chlorure cuivreux ammoniacal. Elle peut s'écrire, en négligeant le rôle de l'ammoniac :

(33) $C_2H_2 + 2\ Cu^+ \rightarrow C_2\ Cu_2 + 2\ H^+$

d'où la mise en évidence d'un caractère acide. Mais cette acidité est très faible ($pK_a \simeq 26$) (8), d'où l'hydrolyse totale des acétylures.

VIII. *Le rôle de l'eau dans la dissociation ionique.*

La dissociation ionique était présentée comme un postulat dans les exposés traditionnels. On n'en explicitait pas les causes ; ou alors, on disait que la constante diélectrique de l'eau ayant une valeur de 80, les forces d'attraction entre ions de signes opposés étaient 80 fois plus faibles, ce qui est un peu formel.

L'explication la plus intéressante est de révéler le caractère faiblement dipolaire des molécules d'eau : la liaison de covalence entre O et H a un caractère partiellement ionique, c'est-à-dire que le doublet électronique commun est plus près de O que de H, bref, tout se passe comme si la molécule d'eau était *légèrement* négative du côté de l'oxygène, et légèrement positive du côté des hydrogènes. Il en résulte vis-à-vis des ions des cristaux, des attractions électriques qui tendent à dissocier les ions. Ces attractions s'exercent aussi sur les molécules à liaison partiellement ionique, comme HCl, d'où également dissociation, et sous forme ionique. La dissociation d'un acide HA en solution dans l'eau est donc une véritable *réaction*, une hydrolyse :

(34) $HA + H_2O \rightarrow A^- + H_3O^+$

H_3O^+ est l'ion hydrogène hydraté (ion hydronium).

En effet, l'ion hydrogène étant un simple proton, peut s'approcher à très courte distance des molécules d'eau qui l'entourent, et les forces électriques sont alors si intenses (loi de Coulomb), qu'il ne peut rester libre (9), et finit par s'y fixer. Les définitions de Brönsted parlent en toute rigueur de *proton,* quand elles l'envisagent dans l'abstrait, et d'ion hydrogène quand elles le considèrent dans son état habituel dans l'eau, c'est-à-dire hydraté. Pour alléger l'écriture, on n'écrit même, chaque fois que cela est possible, que H^+ au lieu de H_3O^+. Mais il importe de ne jamais oublier cette hydratation du proton. C'est de ce point de vue que l'eau, *puisque fixant les protons,* doit être considérée comme une base :

$$(35) \qquad H_2O + H^+ \rightarrow H_3O^+$$

Examinons de plus près la différence avec la théorie d'Arrhénius : Du point de vue traditionnel, la réaction :

$$(36) \qquad H_2O \rightleftarrows H^+ + OH^-$$

donne à l'eau un caractère amphotère du fait de l'apparition simultanée d'ions H^+ (caractère acide) et d'ions OH^- (caractère basique). Notons d'abord que ce terme d'amphotère n'est pas tellement heureux ici, car il s'applique généralement à des corps qui peuvent présenter *une réaction* où ils se comportent comme un acide, et *une autre réaction* où ils se comportent comme une base. *Mais un même comportement n'est pas simultanément acide et basique.* Du point de vue de Brönsted, l'eau est acide dans la réaction (36), et basique dans la réaction (35). Une telle conception est plus satisfaisante, puisque c'est dans deux réactions *différentes* que l'eau a deux comportements différents. Cependant, la réaction (36) nous est plus familière que la réaction (35), et nous hésitons à les mettre sur le même plan ; et puis cette fois, la différence avec le point de vue traditionnel semble trop grand. En fait, c'est notre équation (36) si familière qui traduit incomplètement la réalité. L'eau ne se dissocie pas *sans cause* comme l'implique la réaction (36). Le mécanisme de la dissociation ionique de l'eau étant le même que pour tout autre corps ionisable, une équation telle que (36) représente une dissociation inexplicable, et inexpliquée si on ne fait pas intervenir l'attraction des molécules d'eau *sur les molécules d'eau,* bref si on n'écrit pas au lieu de (35) et (36) :

$$(37) \qquad H_2O + H_2O \rightleftarrows H_3O^+ \quad OH^-$$

Ce n'est pas H_2O qui se dissocie *spontanément,* c'est une première molécule d'eau jouant le rôle de base, qui « arrache » un ion H^+ à une autre molécule d'eau jouant le rôle d'acide. Dans cette réaction unique, nous avons bien *deux comportements différents* des molécules d'eau, définissant ainsi un caractère amphotère, et les deux équations (35) et (36) ne sont que des équations partielles d'un processus global. On retrouve en effet (37) en additionnant (35) et (36).

IX. *pH et théorie de Brönsted.*

C'est incontestablement dans le cadre de la théorie de Brönsted que l'introduction du pH se fait le plus naturellement et le plus logiquement. La similitude des deux conceptions — l'une qualitative, l'autre quantitative — s'affirme dans le rôle primordial qu'elles font toutes deux jouer à l'ion H^+, dans la basicité comme dans l'acidité.

Aujourd'hui, le moindre technicien chimiste ou biologiste utilise le pH. Publicité des produits de beauté, informations de la presse spécialisée sur les mélanges réfrigérants pour radiateurs d'automobile, popularisent la notion. Mais nos élèves de 2^me^, 1^re^ et Math. Elém. continuent de l'ignorer !

Il s'agit pourtant d'une des questions les plus faciles, les plus intuitives, les plus passionnantes, les plus formatrices (10) pour de jeunes chimistes ; et c'est bien pourquoi les valeurs de pH indiquées précédemment pour différents milieux ne doivent absolument pas être considérées comme des données ésotériques, *ad usum magistri,* mais comme des connaissances classiques élémentaires (11).

La notion peut être introduite dès le début du cours de chimie en 2^me^, lors des premières manipulations. L'étude des réactions des deux indicateurs colorés classiques, hélianthine et phtaléine du phénol, sur des solutions plus ou moins diluées d'acide et de base fortes, et sur des solutions d'acides et de bases faibles donnent vite aux élèves la notion d'acidité et de basicité plus ou moins forte, et surtout *une conception unitaire* de ces deux notions. La différence d'action d'un acide borique par exemple (pH = 5), plus commode à employer que l'acide carbonique, sur l'hélianthine (zone de virage 3,1--4,4) et sur la phénolphtaléine (zone de virage 8,3--10) fera comprendre l'utilité d'avoir plusieurs indicateurs, et non un seul, puis sera éclairée par une définition purement pratique du pH : évaluation de l'acido-basicité, variant *à peu près* (12) de 0 à 14, avec neutralité à 7 (à 20° C). Tout ceci soutenu immédiatement par de multiples évaluations de pH de solutions variées, que les plus mauvais élèves arrivent très vite à faire à $\frac{1}{2}$ unité près, en utilisant le papier pH universel 1-10, complété simplement par du papier 9,5-13 pour les bases fortes, et du papier au violet de méthyle (O— 2) pour les acides forts (13). Cette première étude purement expérimentale des acides et des bases facilitera dans le cours sur l'oxygène l'introduction de la distinction entre métaux et non-métaux (métalloïdes), tout en ménageant son caractère relatif.

L'étude de l'acide chlorhydrique, et de la soude approfondira sans les contredire ces premières notions par l'introduction de l'ion H^+. C'est alors que modernisant les classiques dosages acidimétriques, on pourra faire tracer aux élèves la classique courbe de variation du pH lors de la neutralisation de 10 cm^3 d'acide chlorhydrique décinormal par de la soude décinormale en utilisant un indicateur universel liquide. Bien entendu, on disposera de la courbe théorique, tracée sur une feuille de papier millimétrique, pour montrer après aux élèves. L'usage de l'hélianthine ou de la phénolphtaléine pour un dosage acide fort base forte sera ainsi mieux compris. (La même manipulation pourra être reprise en Math. Elém. pour l'acide acétique, les dosages acide faible base forte, et la justification rationnelle de l'emploi de la phtaléine à l'exclusion de l'hélianthine).

Une étape ultérieure (par exemple, lors de l'étude de l'acide carbonique) précisera la différence entre acidité actuelle (pH), et acidité totale (mesurée par les dosages). Le pH sera défini mathématiquement, sans qu'il soit nécessaire de faire appel explicitement aux logarithmes, en posant pour la concentration (actuelle) en ion H^+, comme le fit d'ailleurs Sörensen (14) : $C_{H^+} = 10^{-pH}$, soit en précisant : pH = 1 signifie $C_{H^+} = 10^{-1}$, pH = 2 signifie $C_{H^+} = 10^{-2}$,etc. On renverra aux cours de mathématiques pour l'interpolation des valeurs fractionnaires de pH.

CONCLUSION :

La théorie de Brönsted est plus *traditionnelle* que la théorie d'Arrhénius, n'étant en définitive qu'un retour aux premiers concepts de la chimie, réinterprétés par les théories modernes.

La théorie de Brönsted est plus *naturelle*, car elle est un approfondissement des premières idées intuitives des élèves.

La théorie de Brönsted est plus *concrète*, car elle explique les expériences plus rapidement et plus simplement (par exemple la phtaléine rougie par le carbonate de sodium).

La théorie de Brönsted est *meilleure,* car elle introduit plus d'unité dans nos conceptions, ce qui est l'idéal de toute théorie.

Son application (15) peut se faire avec toute la progressivité et la prudence désirée, rien n'obligeant à en exploiter jusqu'au bout les concepts. On peut même se limiter aux seules définitions, puis en déduire (comme cas particulier) les définitions d'Arrhénius et continuer selon l'exposé classique. Mais on garde à tout instant la possibilité d'élargir les notions.

Il est donc raisonnable de soutenir que son utilisation — à un degré laissé à la liberté de chaque maître — s'impose dès l'enseignement du second Cycle.

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G. Charlot : *L'Analyse qualitative et les réactions en solution.* (Masson, éditeur) Chapitre III.

R.P. Bell : Acids and bases. (Methuen, London).
V. spécialement les chapitres I et II.

Petit livre en anglais, mais très facile à lire, et très clair.

On peut se le procurer notamment, sur commande, à la Librairie des Sciences et Techniques Françaises et Etrangères, 24, rue des Ecoles, Paris-5^e, au prix de 7,65 francs.

Notes

(1) Bulletins N° 468 et N° 470.

(2) Dictionnaire de physique, dédié au Roi, 8^e édition 1781, revue, corrigée, et enrichie des découvertes faites dans cette science depuis l'année 1773, par M. Aimé-Henri Paulian, Prêtre, de l'Académie Royale de Nîmes, et de la Société Royale d'Agriculture de Lyon (4 tomes).

Je dois cette très intéressante référence à notre collègue G. Bonjean.

(3) Le mot « théorie » dans tout cet article sera utilisé au sens d'*étude théorique* comme lorsqu'on parle de la théorie des systèmes centrés, ou de la théorie de la machine à vapeur.

(4) ou en solution dans le benzène (Pascal : Traité de Chimie Minérale).

(5) Pour cette question la considération du pH des solutions clarifie énormément l'exposé. C'est une des raisons qui plaident pour l'introduction de la notion de pH dès les classes élémentaires. Toutes les valeurs numériques indiquées ont été déterminées avec des papiers indicateurs de pH (et vérifiées au moyen des constantes théoriques !).

(6) Recette pratique pour rosir (avec le minimum d'acide) l'hélianthine : Dans un tube à essais ou un verre, mettre plein d'eau, et le moins d'acide possible (avec le flacon, sans s'embarrasser d'une pipette). Agiter et jeter le tout dans l'évier. *Sans rincer*, remplir à nouveau de la quantité d'eau désirée : la solution obtenue ne contiendra d'acide que la très faible quantité, déjà diluée, qui mouillait les parois. Même procédé pour rosir avec le minimum de soude la phtaléine.

(7) C'est de la même manière que les anhydrides (d'acides) qui deviennent des acides en présence d'eau seront intégrés aux acides (P. Marck, p. 338, P. Provost, p. 614).

(8) N.S. Wooding & W.C.E. Higginson, Journal of the Chemical Society (London). On peut consulter cette revue à la Bibliothèque du C.N.R.S. (l'après-midi seulement) 13, quai Anatole-France, Paris-7e.

(9) Les calculs théoriques évaluent à 10^{-210} la concentration possible en proton libre !

(10) les plus formatrices, car elle oblige les élèves à manipuler avec soin et à considérer la chimie comme une science de précision, tout comme la physique.

Les plus passionnantes, car elle s'appuie sur le goût naturel des élèves pour les réactions avec changement de couleur !

(11) Article « Le pH dans l'Enseignement du Second Cycle », revue l'Information Scientifique (éditions Baillère), N° 4 de septembre-octobre 1961.

(12) On sait qu'avec des solutions concentrées d'acide fort on a des pH négatifs, et avec des solutions concentrées de base forte des pH supérieurs à 14.

(13) Le commerce fournit de nombreux indicateurs pH, papier ou liquide, universel ou par zones, de marques françaises ou étrangères : Prolabo, Kuhlmann, Monnet (40, rue Blanche, Paris-9e, pour le papier au violet de méthyle notamment).

(14) Bulletin de l'U.d.P. n° 469, mars-avril 1963, p. 431 et sq. « Réflexions sur la notion de pH » (L. Vareille).

(15) L'introduction de la théorie des ions en 2e n'exige nullement l'étude de la structure de l'atome (la règle de l'octet est complètement inutile pour traiter la structure de l'ion NO_3^- ou SO_4^{--}). La seule notion de charges électriques élémentaires (électrons en excès ou en défaut) porté par un atome ou un groupe d'atomes suffit amplement.

Reprinted from *Bulletin de l'Union des Physiciens*, 1964, pp. 179-18

Ammoniac et sa solution dans l'eau

La molécule d'ammoniac a la forme d'une pyramide dont l'azote est au sommet à la distance x = 0,38 Å du plan des hydrogènes et où l'angle $\widehat{HNH}$ vaut 106°6 (Fig. 1) (1). La courbe d'énergie potentielle de cette molécule en fonction de x est caractérisée par un double minimum (Fig. 2) ; il y a donc deux configurations d'équilibre équivalentes et une barrière de potentiel V_0 (V_0 = 5,9 kcal. mole^{-1}) entre ces deux configurations. Bien que l'énergie de vibration soit inférieure à V_0, le passage d'une configuration à l'autre est possible grâce à l'effet tunnel. C'est ce qu'on appelle l'inversion de la molécule d'ammoniac ; la fréquence d'inversion peut servir d'étalon dans une horloge atomique.

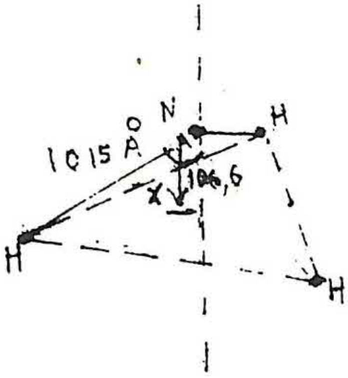


Fig I

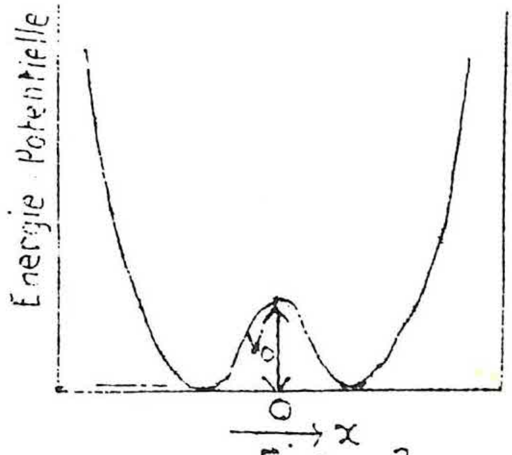


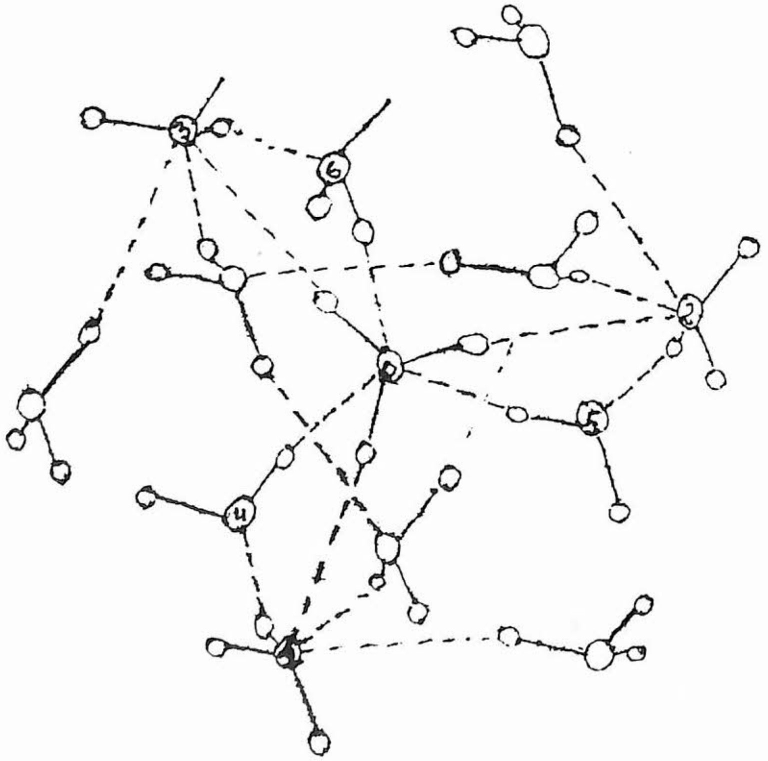
Fig. 2.

Lorsqu'on étudie la molécule d'ammoniac par la méthode des orbitales moléculaires (2), on trouve que l'on peut décrire les dix électrons de la molécule comme suit : deux forment la couche K de l'azote, six forment les liaisons et deux un doublet libre sur l'azote dont l'orbitale correspondante a, pour axe, l'axe Ox de la molécule. Le doublet libre qui occupe ainsi une orbitale hybride fortement dirigée est responsable du moment dipolaire relativement élevé de la molécule d'ammoniac (μ = 1,5 D) ; on peut remarquer que la molécule de trifluorure d'azote NF_3 de même structure que la molécule d'ammoniac a un moment dipolaire de 0,2 D. Dans NH_3, le moment résultant des liaisons N-H se trouve dans une direction opposée à celle du moment dû à l'orbitale occupée par le doublet ; mais le moment dû au doublet est considérablement plus grand et le moment de NH_3 est important. Dans NF_3, le moment résultant des liaisons N-F est beaucoup plus important et le moment total de NF_3 est très petit.

Enfin, l'existence de ce doublet explique les propriétés basiques de NH_3 au sens de la théorie de Brönsted, c'est-à-dire que NH_3 peut fixer facilement un proton :

$NH_3 + H^+ \rightarrow NH_4^+$. L'ion ammonium, ayant la même structure électronique que le méthane, a aussi la symétrie tétraédrique comme cela a été montré par des études de diffraction des neutrons sur des sels d'ammonium (3). La distance N-H vaut **1,03** Å.

Le doublet libre sur l'azote est aussi responsable de la formation de liaisons hydrogènes. En effet, quand on étudie la forme cubique des cristaux d'ammoniac deutéré soit par les rayons X (4), soit par la diffraction des neutrons (5), on trouve que chaque atome d'azote est entouré par six atomes d'azote (situés à 3,35 Å) auxquels il est



Les atomes d'azote 1, 2, 3, 4, 5 sont les plus proches de l'azote central O. — Fig. 3 (d'après J.W. Reed et P.M. Harris, J. Chem. Phys. *35*, 1736 (1961).

lié par liaison hydrogène et six atomes plus lointains, situés à 3,88 Å (Fig. 3). Ces liaisons hydrogènes sont faibles et sont un des rares exemples où les trois atomes compris dans la liaison hydrogène ne sont pas en ligne droite; en effet, l'angle N-- D--- N a une valeur de 164° ± 1,7°.

Les molécules d'ammoniac peuvent aussi former des liaisons hydrogènes avec l'eau. Ceci se voit tout d'abord nettement dans la structure cristalline des hydrates de l'ammoniac. En effet, NH_3 forme deux hydrates solides NH_3, H_2O et 2 NH_3, H_2O, tous deux formés à basse température et qui sont *instables*. Dans le cristal de NH_3, H_2O (6), les molécules d'eau sont liées par des liaisons hydrogènes en des chaînes et les molécules d'ammoniac forment des liaisons hydrogènes avec ces molécules d'eau, donnant ainsi naissance à un réseau tridimensionnel.

Il n'y a pas de liaisons hydrogènes entre molécules d'ammoniac.

La structure cristalline de 2 NH_3, H_2O a été étudiée à 170° K (7). Le cristal est formé d'un squelette de composition NH_3, H_2O, contenant des liaisons hydrogènes ; NH_3 et H_2O forment chacun une liaison hydrogène forte où la distance N...H-O vaut 2,84 Å et trois liaisons plus faibles (distances N...H-O = 3,13 Å 3,22 Å et 3,22 Å). La deuxième molécule de NH_3 est attachée à ce squelette seulement par une seule liaison N-H-O de type liaison hydrogène (distance N-H-O = 2,84 Å).

Avant ces résultats relativement récents, de nombreux auteurs avaient suggéré que la structure cristalline de ces hydrates était du type ionique c.a.d. qu'ils étaient formés d'ions NH_4^+ et d'ions OH^-. En fait, Waldron et Hornig (8) avaient montré que les spectres infra-rouges de ces hydrates sont très proches de ceux de l'ammoniac et de l'eau et annoncé que les deux hydrogènes de chaque molécule d'eau forment des liaisons hydrogènes.

Dans le cas de la solution aqueuse de NH_3, *l'interaction entre NH_3 et l'eau est faible.*

Le spectre infra-rouge de solutions aqueuses d'ammoniac ressemble beaucoup à celui de l'ammoniac liquide anhydre. On observe simplement de légers déplacements des bandes; par exemple, le deuxième harmonique de la fréquence fondamentale (c.a.d. $3\nu_{N-H}$) a les valeurs suivantes (9) :

NH_3 liquide	9568 cm^{-1}
solution aqueuse 20 %	9622 cm^{-1}
gazeux	9688 cm^{-1}

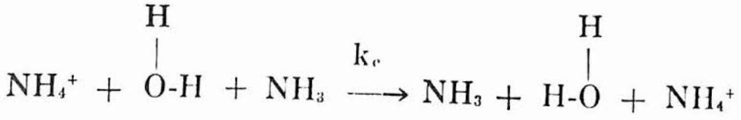
De même, le spectre Raman (10) de l'ammoniac en solution aqueuse est très semblable à celui de NH_3 liquide anhydre (ν_{N-H} = 3310 cm^{-1} pour NH_3 liquide et ν_{N-H} = 3314 cm^{-1} pour NH_3 en solution aqueuse).

Ces résultats suggèrent la possibilité de formation de liaisons hydrogènes; il y a deux possibilités de formation de liaisons hydrogènes dans la solution d'ammoniac dans l'eau : N-H...O et N...H-O. L'azote est un meilleur accepteur (propriétés basiques de NH_3) que l'oxygène et le groupement OH est un meilleur donneur que NH (11). C'est donc uniquement le type de liaisons hydrogènes N...H-O que l'on trouve dans les solutions d'ammoniac et dans les cristaux de NH_3, H_2O et NH_3, H_2O.

L'étude de la variation des fréquences de résonance magnétique nucléaire avec la concentration (12) a permis de montrer que l'interaction entre NH_3 et H_2O existe, qu'elle est du type liaison hydrogène et que chaque liaison hydrogène n'a pas un temps de vie supérieur à 10^{-8} s. Ces dernières années, les solutions de sels d'ammonium ou de sels d'amine ont été très étudiées par R.M.N. (12) (13) pour tirer au clair le mécanisme de l'échange du proton entre NH_4^+ et H_2O et la constante de vitesse de la rupture de la liaison hydrogène. Ainsi par l'étude de solutions de chlorure d'ammonium en milieu acide, les constantes de vitesse ont été déterminées pour les réactions :

$$\mathrm{NH_3 + H_3O^+ \xrightarrow{k_a} NH_4^+ + H_2O}$$

$$\mathrm{NH_4^+ + NH_3 \xrightarrow{k_b} NH_3 + NH_4^+}$$



$$\mathrm{NH_4^+ + \overset{H}{\overset{|}{O}}\text{-}H + NH_3 \xrightarrow{k_c} NH_3 + H\text{-}\overset{H}{\overset{|}{O}} + NH_4^+}$$

Les valeurs suivantes ont été trouvées :

$k_a = 4{,}3 \times 10^{10}\ s^{-1}\ M^{-1}$, $k_b = 1{,}17 \times 10^9\ s^{-1}\ M^{-1}$ et

$k_c = 0{,}9 \pm 1{,}0 \times 10^8\ s^{-1}\ M^{-1}$. Ces réactions sont donc extrêmement rapides. On trouve aussi une constante de vitesse du même ordre de grandeur ($k = 51 \times 10^{10}\ s^{-1}$) pour la rupture de la liaison hydrogène H_3N... HOH (12). Des résultats identiques ont été trouvés récemment pour des amines (14).

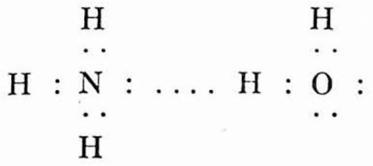
Enfin toujours par des techniques de résonance nucléaire, on peut trouver les énergies d'activation des réactions :

$$NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+ \qquad (1)$$

et $$NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O \ (11).$$

L'énergie d'activation de la réaction I a été trouvée égale à 12,2 kcal mole^{-1} tandis que celle de la réaction II a été trouvée à peu près nulle. Ainsi des rôles semblables sont joués par NH_4^+ et H_3O^+ mais NH_3 est un meilleur accepteur de proton que H_2O (15).

En conclusion, on peut adopter le point de vue suivant : il n'est pas possible d'écrire une formule covalente contenant un azote pentavalent et qui représenterait la molécule NH_4OH. Il semble que parler de NH_4OH ne peut que fausser les idées de débutants en chimie et qu'il n'existe entre la molécule d'ammoniac et celle de l'eau qu'une interaction faible du type liaison hydrogène. Ces interactions varient très rapidement. Ainsi la molécule d'hydrate d'ammoniac peut être représentée comme suit :



$$\begin{array}{ccccccccc} & & H & & & & & H & \\ & & \cdot\cdot & & & & & \cdot\cdot & \\ H & : & N & : & \ldots\ldots & H & : & O & : \\ & & \cdot\cdot & & & & & \cdot\cdot & \\ & & H & & & & & & \end{array}$$

La liaison hydrogène est une liaison beaucoup plus faible que la liaison covalente (énergie de liaison de l'ordre de 5 kcal/mole c.a.d. de l'ordre de dix fois plus faible qu'une énergie de liaison covalente) et ceci explique l'instabilité de l'hydrate d'ammoniac $NH_3 . H_2O$ et le fait qu'il n'existe pas à la température ordinaire.

Dans l'équilibre :

$NH_3 + H_2O \rightleftarrows NH^+_4 + OH^-$, les ions NH_4^+ et OH^- interagissent sûrement plus fortement avec le solvant que ne le fait la molécule NH_3. Il n'y a pas plus de raison de tenir compte de la solvatation pour NH_3 que pour les ions NH_4^+ et OH^-. Aussi, on définit la constante d'acidité de l'ion NH_4^+ par $K_A = \dfrac{[NH_3]\ \ [H_3O^+]}{[NH_4^+]}$ où NH_3 représente la concentration totale de l'ammoniac non ionisé dans la solution, sans tenir compte de l'hydratation. De même, quoique la tendance actuelle soit de ne plus utiliser les constantes de basicité mais celles d'acidité des acides conjugués, on définit la constante de basicité :

$$K_B = \frac{[NH_4^+]\ [OH^-]}{[NH_3]}$$

où $[NH_3]$ a la même signification que précédemment (16) (17).

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Signs of Tensions in Electrochemistry

Two international commissions, working jointly much of the time, have been trying since 1950[1] and 1953,[2] respectively, to clarify the peculiarly confused domain of definitions of fundamental electrochemical concepts, electrochemical nomenclature, so-called "sign conventions," etc. These commissions took part in the discussions which led to the 1953 Stockholm "conventions concerning the sign of electromotive forces and electrode potentials." They gave their approval to the text which was published jointly by the chairmen of the Commission on Physico-Chemical Symbols and Terminology and of the Commission on Electrochemistry of the IUPAC (*1*) and republished several times since (*2*, *3*).[3] This approval was meant essentially for the settlement, once and for all it was hoped, of the matter of the signs of electrode potentials (the standard electrode potential of the Zn|Zn^{2+} electrode is −0.76 v, not + 0.76 v). However, the two electrochemical groups have continued their efforts toward clarification and extensive reports on the whole subject have been published (*4*) and commented upon (*7*). The present author and his colleagues of the commissions have repeatedly noticed that in much of the current literature the Stockholm recommendations are sometimes not observed and often misunderstood or misquoted, and that the precise definitions which have been established over these many years are still insufficiently known. In addition there have been occasional objections against the use in English of the various "tensions" (electrochemical, electric, chemical) which appear to be accepted in all other languages.

The present paper is an attempt by the chairman of these commissions (acting alone but with the support of his colleagues) to connect the present state of the commissions' work with current practice in textbooks and elsewhere.

We shall take as point of departure the classical textbook formula

$$\Delta G = -z\,\mathfrak{F}\,E \tag{1}$$

connecting the so-called *electromotive force* E of a galvanic cell with the change in *Gibbs energy* (or *free enthalpy*) G corresponding to one occurrence of the cell reaction, z being the number of faradays $\mathfrak{F}$ involved in the reaction. This formula is derived for reversibility and for given temperature and pressure. To see clearly what ΔG and E really are we take, for instance, the cell

$$\begin{array}{ccccccccccc} \mathrm{Cu} & | & \mathrm{Zn} & | & \mathrm{Zn^{2+}} & || & \mathrm{Ag^+} & | & \mathrm{Ag} & | & \mathrm{Cu} \\ a & & 1 & & 2 & & 3 & & 4 & & b \end{array} \tag{2}$$

consisting of the metal-solution electrode Zn|Zn^{2+} and the solution-metal electrode Ag$^+$|Ag and of the copper leads a and b. The double bar between phases 2 and 3 represents the liquid junction whose electric potential difference will be neglected or assumed corrected for. If a positive current I passes through the cell from left to right the following reaction takes place from left to right as written:

$$\mathrm{Zn} + 2\,\mathrm{Ag}^+ + 2\,e^-(b) \rightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{Ag} + 2\,e^-(a) \tag{3}$$

At electrochemical equilibrium we have, in terms of the chemical potentials μ and of the electric potentials φ:

$$\mu_{\mathrm{Zn}} + 2\,\mu_{\mathrm{Ag}^+} - 2\,F\,\varphi^b = \mu_{\mathrm{Zn}^{2+}} + 2\,\mu_{\mathrm{Ag}} - 2\,F\,\varphi^a \tag{4}$$

since the chemical potential of the electron is the same in a and b and since the difference $\varphi^2 - \varphi^3$ is neglected or corrected for.

Comparing (1) and (4) we find:

$$\Delta G = \mu_{\mathrm{Zn}^{2+}} + 2\,\mu_{\mathrm{Ag}} - \mu_{\mathrm{Zn}} - 2\,\mu_{\mathrm{Ag}^+} \tag{5}$$

$$E = (\varphi^b - \varphi^a)_{rev} \tag{6}$$

in which the subscript *rev* indicates reversibility.

We thus see that the actual meaning of (1) is that the condition of electrochemical equilibrium of the cell is:

$$(\varphi^a - \varphi^b)_{rev} = \Delta G/z\,\mathfrak{F} = -E \tag{7}$$

or

$$(\varphi^a - \varphi^b)_{rev} + E = 0 \tag{8}$$

which shows that the *reversible electric tension* $U_{rev} = (\varphi^a - \varphi^b)_{rev}$ is balanced by the *chemical tension* or *electromotive force* E:

$$U_{rev} + E = 0 \tag{9}$$

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[1] CITCE Commission on Electrochemical Nomenclature and Definitions. CITCE = Comité International de Thermodynamique et de Cinétique Electrochimiques" (International Committee of Electrochemical Thermodynamics and Kinetics), created in 1949, an affiliated commission of the IUPAC[2] for many years.

[2] IUPAC Subcommission on Electrochemical Symbols and Terminology of the Commission on Electrochemistry. IUPAC = International Union of Pure and Applied Chemistry. The recommendations referred to in the present paper are endorsed by the whole CITCE Committee, but, as far as IUPAC is concerned, they are, for the time being, only those of the Commission on Electrochemistry, which hereby and through its published reports (*4*) invites comments from all interested parties.

[3] Licht and de Béthune (*2*) gave an interesting and valuable review of the whole problem, but their discussion did not include in an explicit manner formulas of the type of our formulas (9) and (13) which we consider as crucial to a direct and clear understanding of the subject. Such formulas easily settle the point raised by Anson (*5*). As to the concept of "electron chemical potential" brought up by Ramsey (*6*) it will be found treated in a straightforward manner in section 4.13 of the CITCE report (*4*)

with E given by:

$$E = -\Delta G/z\,\mathfrak{F} = A/z\,\mathfrak{F} \qquad (10)$$

in which A is the *chemical affinity* of the cell reaction. If, keeping the diagram of the cell given in (2) but writing the reaction given in (3) in the opposite direction, the number of faradays carried from left to right in the cell during one occurrence of the reaction would now be -2. There would then be simultaneous changes of sign for ΔG and z or for A and z and it is thus seen that U_{rev} and E are invariant in magnitude and in sign with respect to this reversal in the writing of the cell reaction.

Outside of equilibrium, i.e., with passage of current, U differs from U_{rev} on account of ohmic drops within the cell and of polarization at the electrodes, while E remains constant, at given temperature and pressure, as long as the composition of the phases is not altered.

Let us now replace the right-hand electrode of cell (2) by the standard hydrogen electrode:

$$\underset{a}{\mathrm{Cu}}|\underset{1}{\mathrm{Zn}}|\underset{2}{\mathrm{Zn^{2+}}}||\underset{3}{\mathrm{H^+}\,(a_{\mathrm{H^+}} = 1)}|\underset{4}{\mathrm{Pt,\ H_2}\,(p_{\mathrm{H_2}} = 1\ \mathrm{atm})}|\underset{b}{\mathrm{Cu}} \qquad (11)$$

Reaction (4) is now replaced by:

$$\mathrm{Zn} + 2\,\mathrm{H^+}\,(a_{\mathrm{H^+}} = 1) + 2\,e^-(b) \rightarrow \mathrm{Zn^{2+}} + \mathrm{H_2}\,(p_{\mathrm{H_2}} = 1\ \mathrm{atm}) + 2\,e^-(a) \qquad (12)$$

The electric tension U_{rev} is now the *electrode potential* (in the Stockholm sense) of the $\mathrm{Zn}|\mathrm{Zn^{2+}}$ electrode, while the chemical tension or emf E is now what has commonly been called the *oxidation potential*. A precise appellation for this quantity is *oxidation affinity per coulomb*. We have:

$$U_{rev} + E_{oxid} = 0 \qquad (13)$$

If we place the standard hydrogen electrode on the left-hand side of the cell we have the following diagram:

$$\mathrm{Cu}|\mathrm{Pt,\ H_2}|\mathrm{H^+}||\mathrm{Zn^{2+}}|\mathrm{Zn}|\mathrm{Cu} \qquad (14)$$

with, in place of (13):

$$U'_{rev} + E_{red} = 0 \qquad (15)$$

in which the chemical tension or emf E_{red} is now what has commonly been called the *reduction potential*. A precise appellation for this quantity is *reduction affinity per coulomb*. However, U'_{rev} may *not* be called electrode potential, while the actual electrode potential U_{rev} of formula (13) is thus related to E_{oxid} and E_{red} as follows:

$$U_{rev} = -E_{oxid} = E_{red} \qquad (16)$$

For the standard $\mathrm{Zn}|\mathrm{Zn^{2+}}$ electrode we have $U°_{rev} = -0.76$ v, $E°_{oxid} = +0.76$ v, $E°_{red} = -0.76$ v.

The foregoing discussion shows that it is advisable to give in textbooks the electromotive series with three columns of data corresponding to $U°_{rev}$, $E°_{oxid}$, and $E°_{red}$. This should clear up, among other matters, the old but persistent lore concerning so-called European and American signs or European and American conventions.

Out of equilibrium the sum $U + E$ is not equal to zero any more. It is now equal to what may be called the *electrochemical tension* of the cell:

$$\tilde{E} = U + E \neq 0 \qquad (17)$$

a quantity equal, in the case of a positive current passing from left to right inside the cell, to the sum of three positive terms: the ohmic drop in the cell, the *anodic overtension* at the $\mathrm{Zn}|\mathrm{Zn^{2+}}$ electrode and the absolute value of the *cathodic overtension* at the $\mathrm{Ag^+}|\mathrm{Ag}$ electrode in the case of cell (2). If the current from left to right is negative $\tilde{E}$ is equal to the sum of three negative terms: minus the ohmic drop from right to left in the cell, the cathodic overtension at the $\mathrm{Zn}|\mathrm{Zn^{2+}}$ electrode and minus the anodic overtension at the $\mathrm{Ag^+}|\mathrm{Ag}$ electrode. The product of $\tilde{E}$ by the current is thus always positive and equal to the power of irreversibility of the cell, itself equal to the entropy production per unit time multiplied by the absolute temperature (*8*). It should be clear that the relative electric tension of an electrode (or its electrode potential, equal to the electric tension of cell (11) in the case of $\mathrm{Zn}|\mathrm{Zn^{2+}}$) moves toward more positive (or less negative) values than the equilibrium one when the electrode functions anodically and toward less positive (or more negative) values when the electrode functions cathodically.

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Section 8 Elements and their compounds

Most of the articles in this section have been chosen to show how the new trends in chemistry have influenced the way in which the systematic chemistry of the elements can be presented.

The field of noble gas chemistry is being very actively investigated. The paper by N. Greenwood summarizes the position as it was in 1964. Controversy still continues over the structure of XeF_6 and the bonding in this molecule. Other helpful articles on this topic are H. H. Hyman's "The Chemistry of Noble Gases", *Journal of Chemical Eaucation*, 1964, p. 174, and C. L. Chernick's "The Noble Gas Compounds", *Chemistry*, Vol. 37, 1964, p. 6.

Reprinted from *Chemistry*, Vol. 37, No. 2, 1964, pp. 7-11.

Chemistry deals with matter and its transformations, but seldom does a chemistry course deal with the formation and transformations of the elements themselves. This is probably traditional, for Dalton and many after him believed that the elements were unchangeable. Perhaps the chemistry books of the future will begin with an article something like the one presented here—Part I this month, Part II to follow in an early future issue.

ORIGIN AND EVOLUTION OF CHEMICAL ELEMENTS

David P. Mellor *University of New South Wales, Kensington, Australia*

To most chemists of the 19th century, the question of the origin of the elements would have had little meaning since, to them, the atom was indivisible, immutable, and everlasting. One notable exception to this statement was William Prout, a doctor of medicine practicing in London, who in 1815 propounded the view that all atomic weights are exact multiples of that of hydrogen and that hydrogen is the primary substance or "first matter." He was wrong on the first point but remarkably close to the modern view on the second for we now believe that hydrogen *is* the raw material from which the process of element building begins. One of the important consequences of Mendeleev's discovery of the Periodic Law was the emergence of the belief that the chemical elements are not fragmentary, incidental facts of nature but successive units in the harmony of the universe.

Atoms are complex structures, consisting of a positively charged nucleus and a cloud of surrounding electrons whose charge is equal but opposite to that on the nucleus. The nucleus itself is complex, consisting of a tight combination of protons and neutrons. A nucleus is specified by the number of protons, Z, which determines its charge, and the number of neutrons, N. Its mass number, A, is the sum of Z plus N. The charge on the nucleus, Z, known as the atomic number, determines the number of planetary electrons, and it is the number and arrangement of these that determine the chemical behavior of an atom. Each element is characterized by its atomic number. Nuclear species (nuclides) with the same atomic number (Z) but different numbers of neutrons, and hence different mass numbers A, are known as isotopes. In the recurrence of similar electronic configurations, as we progress from the simplest to the most complicated atoms, is found an explanation of the recurrence of similar chemical behavior among the elements.

Perhaps the most significant of all discoveries with a bearing on the problem of the origin of the elements was that made by Rutherford in 1917. He showed then that the nucleus of one atom (nitrogen) could be transformed into the nucleus of another (oxygen) by bombardment with swift α particles (helium nuclei):

$$N^{14} + He^{4} \rightarrow O^{17} + H^{1}$$

Since that momentous discovery many hundreds of nuclear transformations have been achieved by bombarding atoms with different kinds of particles—protons, deuterons, α particles, and neutrons. Transmutation of elements by nuclear reactions is the key to an understanding of their origin and evolution. The formation of the elements is a matter of the synthesis of their nuclei.

Cosmochemistry, the chemistry of the universe, has as one of its main aims the determination of the "cosmic" abundance of the elements. Any satisfactory theory of the origin of the elements must explain their cosmic abundance. Indeed, many clues as to the nature of the processes involved in nucleosynthesis are found in the relative abundance of the elements. Chemical analysis of the universe is, of course, an impossible task. When a chemist sets out to analyze a large pile of mineral concentrates, for example, his first care is to obtain a representative sample of the material. This most important operation is also the major concern of the cosmochemist who sets out to determine the cosmic abundance of the elements. He is, however, more restricted than the assayer in the range of his

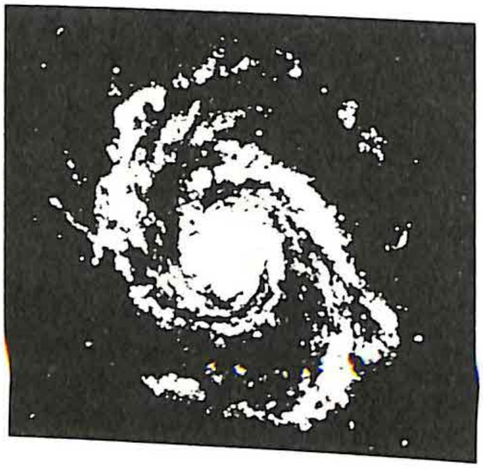


Figure 1. Spiral nebula in Canes Venatici

sampling. He cannot sample the whole universe because it is so unimaginably vast.

The known universe is populated by millions of huge star systems known as galaxies or "island universes," each of which is an assembly of many thousands of millions of stars. "The galaxies stretch away from us farther and farther into space and by the time they are lost to view (through faintness due to great distance), some 100 million or more of them are accounted for" (*3*). Since the sun lies well within the confines of our own galaxy (the Milky Way), we are unable to see what the system looks like as a whole. Nevertheless, there is very good evidence that the Milky Way has a spiral structure like that of the nebula shown in Figure 1. Not all nebulae have this shape; some are quite irregular.

The best the cosmochemist can do is to sample small portions of the galaxy, concentrating mainly on the sun, which is an average star, and on some of its nearest and brightest neighbors. Only the brightest stars produce spectra suitable for detailed chemical analysis. This limitation on sampling means that we are making a vast extrapolation in using the term "cosmic abundance."

The principal sources of information from which the cosmic abundance of the elements has been derived are the earth's crust, meteorites, the sun and bright stars, and gaseous nebulae. When considering any of these sources, the influence of its previous chemical and physical history on its composition must be constantly borne in mind. No attempt will be made to discuss any of these sources in detail. But data relating to the sources will be examined from the point of view of their bearing on the problem of nucleosynthesis.

Atomic Weights

C	12.0
O	16.0
Mg	24.3
Si	28.1
S	32.1
Ca	40.1
Fe	55.8

Atomic Numbers

O	8
Mg	12
Al	13
Si	14
S	16
Ca	20
Fe	26
Ni	28

Abundance of the Elements

The Earth's Crust. It was natural that the abundance of the elements in the earth's crust should have been studied first. The earliest study was made in 1889 by Clarke (*1*), who based his estimates on an extensive series of rock analyses. He plotted abundances of the elements against atomic weights, hoping to find periodicities related to those of the Periodic Table, but he found none. We know now that there is no reason to expect periodicities of this kind; there is no reason why the abundance of an element should depend on its chemical properties. Modern work shows that there *are* periodicities in the abundance of the elements but of a different kind. As we shall see later, they are related to the properties of the nucleus.

Results of the most recent estimates of the abundance of the most common elements in the earth's crust are given in Table I. Oxygen dominates the picture. Eight elements, all of them light elements—O, Si, Al, Fe, Ca, K, Na, and Mg—make up 98% of the crust. These are followed by Ti, P, H, and Mn in that order. All the remaining elements contribute less than 0.6%.

Two interesting regularities have been noticed—the first by G. Oddo in 1914, who pointed out that the elements which make up most of the earth's crust are those whose atomic weights, when rounded off to whole numbers, are divisible by four (C, O, Mg, Si, S, Ca, etc.). Another rule, found in the first instance to apply to meteorites but later also to the earth's crust, was stated by W. D. Harkins in 1917. He noticed that the six most abundant elements found in some 400 meteorites all had *even* atomic *numbers*.

The question arises: Is the earth's crust a representative sample of cosmic matter? The answer is definitely "no." We do not know that it is even a representative sample of the

TABLE I.

Average Composition of the Earth's Crust and Meteoritic Matter

Earth's Crust		Meteoritic Matter	
Element	Weight per cent	Element	Weight per cent
O	46.6	O	32.3
Si	27.2	Fe	28.8
Al	8.13	Si	16.3
Fe	5.00	Mg	12.3
Ca	3.63	S	2.12
Na	2.83	Ni	1.57
K	2.59	Al	1.38
Mg	2.09	Ca	1.33

earth as a whole. Indeed, there are good grounds for suspecting that it is not. Furthermore, there is reason to believe that during its very early history the earth lost a large proportion of its volatile elements—hydrogen, helium, and other rare gases, nitrogen (as NH_3), and some oxygen (as H_2O). In our search for a representative sample of cosmic matter, we turn next to meteorites.

Meteorites. Some scientists believe that meteorites are the fragmentary remnants of a small planetary body of about the size of the moon or smaller. The fragments are of several kinds —the irons (siderites), the stony irons (siderolites), and the stones (aerolites). These are the only samples of matter from outside the earth available for analysis in the laboratory. The class of stony meteorites known as chondrites is thought to be most nearly representative of meteoritic matter, the average composition of which is shown in Table I.

To the question of whether meteoritic matter is representative of "cosmic" matter, the answer is also "no." Meteoritic matter, like the earth's crust, has lost much of its content of volatile elements. Nevertheless, since presumably all parts of the parent planetary body are represented in the specimens available to us, meteoritic matter provides a more nearly representative sample than does the earth's crust of the nonvolatile matter from which the solar system has been formed.

The Sun and Stars. A great deal of work has been done on the spectroscopic analysis of the sun. Table II shows the relative abundance of the more common elements in the solar atmosphere. The results are expressed in terms of atoms per 10,000 atoms of silicon.

Some 66 of the elements up to uranium have been observed in the sun, and there is no reason to conclude that any elements up to number 92, except possibly 43, 61, 85, and 87, are absent. The most striking feature of Table II and one which distinguishes it from Table I is the extreme abundance of hydrogen and helium. This marked difference is attributed to the fact that the sun, unlike the earth and the meteorites, has not lost its volatile elements. Once again, the light elements dominate the picture. Of the 11 most abundant elements, 10 have atomic numbers ranging from 1 to 16; the 11th (iron, atomic number 26) stands by itself in a notable peak. However, all of the light elements are not abundant. There are three outstanding exceptions—lithium, beryllium, and boron.

TABLE II.

Abundance of Elements in the Sun's Atmosphere (*4*)

Element	Abundance, Atoms per 10,000 Atoms of Silicon	Element	Abundance, Atoms per 10,000 Atoms of Silicon
H	5.1×10^8	Ca	870
He	1×10^8	Sc	1.1
C	10,000	Ti	47
N	21,000	V	5.9
O	2.8×10^6	Cr	200
Na	1,000	Mn	150
Mg	17,000	Fe	27,000
Al	1,100	Co	55
Si	10,000	Ni	470
S	4,300	Cu	8.7
K	81	Zn	31

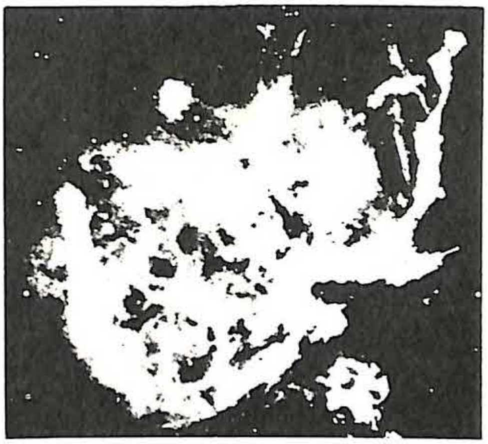


Figure 2. The gaseous nebula in Orion

The sun derives its energy from the "burning" of hydrogen to helium, a process which takes place in the core of the sun where it is believed the temperature is in the neighborhood of 15 × 10^6 °K. There appears to be little diffusion between the hot center and the cooler outer layers of the sun. The composition of the latter is generally thought to represent, fairly closely, the primordial composition of the solar system.

Gas Nebulae and Interstellar Gas. Not all nebulae are vast assemblies of stars. Some are large glowing masses of gas. The atoms in these are excited by ultraviolet radiation from intensely hot stars located within the nebula itself. Figure 2 is a photograph of a gaseous nebula. Spectrum analysis reveals that these bodies also consist mainly of hydrogen (about 65%) and helium (most of the remainder).

The space between stars is not a perfect vacuum. It is filled with a highly tenuous gas and dust—the interstellar medium—from which new stars are eventually formed. The composition of the interstellar medium is not

TABLE III.

Elemental Abundances in the Universe

Element	Atomic Number	Abundance, Atoms per 10,000 Atoms of Silicon	Element	Atomic Number	Abundance, Atoms per 10,000 Atoms of Silicon	Element	Atomic Number	Abundance, Atoms per 10,000 Atoms of Silicon
H	1	4.0×10^8	Cu	29	2.1	La	57	0.020
He	2	3.1×10^7	Zn	30	4.9	Ce	58	0.023
Li	3	1.0	Ga	31	0.11	Pr	59	0.004
Be	4	0.20	Ge	32	0.51	Nd	60	0.014
B	5	0.24	As	33	0.04	Pm	61	—
C	6	35,000	Se	34	0.68	Sm	62	0.007
N	7	66,000	Br	35	0.13	Eu	63	0.002
O	8	215,000	Kr	36	0.51	Gd	64	0.007
F	9	16	Rb	37	0.07	Tb	65	0.001
Ne	10	86,000	Sr	38	0.19	Dy	66	0.006
Na	11	440	Y	39	0.09	Ho	67	0.001
Mg	12	9,100	Zr	40	0.55	Er	68	0.003
Al	13	950	Nb	41	0.01	Tm	69	0.0003
Si	14	10,000	Mo	42	0.02	Yb	70	0.002
P	15	100	Tc	43	—	Lu	71	0.0005
S	16	3,750	Ru	44	0.015	Hf	72	0.0004
Cl	17	90	Rh	45	0.002	Ta	73	0.0007
Ar	18	1,500	Pd	46	0.007	W	74	0.005
K	19	32	Ag	47	0.003	Re	75	0.001
Ca	20	490	Cd	48	0.009	Os	76	0.010
Sc	21	0.28	In	49	0.001	Ir	77	0.008
Ti	22	24	Sn	50	0.013	Pt	78	0.016
V	23	2.2	Sb	51	0.002	Au	79	0.001
Cr	24	78	Te	52	0.047	Hg	80	0.003
Mn	25	69	I	53	0.008	Tl	81	0.001
Fe	26	6,000	Xe	54	0.040	Pb	82	0.005
Co	27	18	Cs	55	0.005	Bi	83	0.001
Ni	28	270	Ba	56	0.037	Th	90	0.0004
						U	92	0.0001

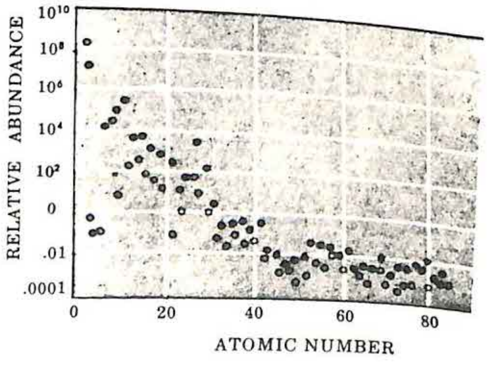
known very accurately. Here again, however, hydrogen and helium are the main components in the ratio of about 10:1. Carbon, oxygen, and nitrogen make up about 1%. Calcium, sodium, potassium, and titanium have also been detected. Neutral atoms of hydrogen present in the interstellar medium emit the 21-cm. spectrum line. Studies of this radiation, made with the help of radiotelescopes have revealed that atomic hydrogen is concentrated in the spiral arms of the galaxy.

By combining data from all the sources just described, V. M. Goldschmidt in 1937 compiled the first table of cosmic abundances. His table has since been modified as more and more information has become available. Table III, one of the most recent, has been compiled by Suess and Urey (*7*).

Hydrogen accounts for 93% of the atoms and 76% of the weight of the universe. Helium is next, accounting for 7% of the atoms and 23% of the weight. Only 10 elements—H, He, C, N, O, Ne, Mg, Si, S, and Fe—all with atomic numbers less than 27, show appreciable abundance. All of the elements beyond helium make up only a little more than 1% of the mass of the universe. In Figure 3, the logarithm of the relative abundance is plotted against atomic number.

As shown in Figure 3, abundance decrease roughly exponentially with increasing atomi number up to about 40; thereafter, there i very little change in abundance. Lithium beryllium, and boron lie outside the mai trend being cosmically far less abundant tha all the other light elements. Elements of eve atomic number are more abundant tha those of odd atomic number on either sid An element may be a hundred or a thousan times more or less abundant than its immed

Figure 3. Relative abundances of the elements plott against atomic number. ○ Elements of odd ator number, ● elements of even atomic number



ate neighbor in the Periodic Table. For example, light elements whose rounded-off atomic weights are divisible by four—C, O, Ne, Mg, Si, S, Ar, Ca, and Fe—are much more abundant than their immediate neighbors (see Table III).

Theories of the Origin of the Elements

Gamow's Theory. This theory (2) sometimes referred to as the primordial or "big bang" theory, assumes that the universe began as an exceedingly dense mass of neutrons. "In the beginning" was a vast explosion. As the mass began to expand, some of the neutrons decayed to protons and electrons:

$$n \rightarrow p + e.$$

Protons combined with neutrons to form deuterium (H^2) nuclei, and these in turn combined with neutrons to form tritium (H^3), both processes being accompanied by emissions of γ-radiation:

$$p + n \rightarrow H^2 + \gamma$$
$$H^2 + n \rightarrow H^3 + \gamma$$

Neutron capture continued apace, forming successively the nuclei of all the elements. The whole process took place, so the theory states, in a matter of minutes and the exploding matter formed the receding galaxies.

Several observations seemed to support Gamow's beautifully simple theory, and laboratory experiments show that nearly all kinds of nuclei do readily combine with neutrons—some kinds much more readily than others. They do so by what is called the $n\ \gamma$ reaction—an unstable nucleus formed by capture of a neutron decays to a stable nucleus by the emission of a β particle (electron). Among the heaviest elements, the conversion of gold to mercury is a good example:

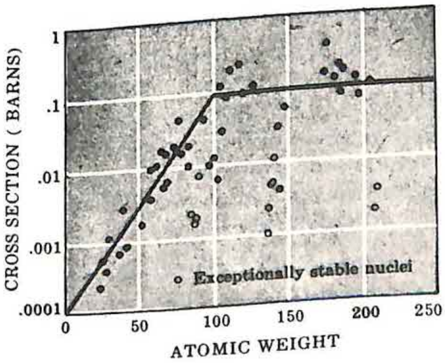
$$ {}_{79}\mathrm{Au}^{197} + n \rightarrow {}_{79}\mathrm{Au}^{198} + \gamma$$
$$ {}_{79}\mathrm{Au}^{198} \rightarrow {}_{80}\mathrm{Hg}^{198} + {}_{-1}e^{0}$$

Nuclei that combine readily with neutrons are said to have a large capture cross section. Such nuclei should be rarer than those that do not combine so readily since the reactive nuclei are rapidly converted to succeeding nuclei. Consequently, the curve (Figure 4) formed by plotting neutron capture cross section against atomic mass, should be the inverse of the abundance curve shown in Figure 3.

Despite this seemingly favorable evidence, Gamow's theory proved to have a fatal flaw. There are no stable nuclides with mass numbers five and eight respectively. If neutron capture were the only process by which elements could be formed in nature, it would be impossible to bridge the gaps five and eight. Element formation would therefore stop with helium. Gamow's theory is in general, therefore, not now highly favored.

To be continued

Figure 4. **Plot of nuclear cross sections for neutron capture, measured in barns (one barn equals 10^{-24} sq. cm.), *vs.* atomic weight. The heavier nuclei capture neutrons more readily. The exceptionally stable nuclei are indicated by open circles [Reproduced from *Scientific American*, 195, p. 85 (September 1956), with permission of the publishers]**



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Origin and Evolution of Chemical Elements

part 2

David P. Mellor, *University of New South Wales, Kensington, Australia*

An introduction to the nuclear transformations believed to occur in the interiors of stars, and an extrapolation backward in time to the origin of the elements.

In Part I of this article (CHEMISTRY, February 1964, page 7) procedures were described for estimating abundances of different elements in the universe. One theory of chemical evolution was discussed to account for these abundances but could not adequately explain them.

Formation of Elements in Stars

The now generally accepted theory (*9*), which is a good deal more complicated (it invokes at least eight different kinds of nuclear processes, six of which are discussed here), is based on two main assumptions—namely, that the raw material for element building is hydrogen, the most abundant material in the universe, and that the elements are formed in the interior of stars. It also assumes that a first generation star is born from a cold gaseous mass of hydrogen atoms. Under the influence of gravity, the mass slowly contracts, and as it does, gravitational energy is converted to heat, and the temperature of the interior rises until it reaches about five million degrees. This heat is sufficient to induce a thermonuclear reaction—the fusion of protons.

At temperatures about 5×10^6 °K., protons have sufficient kinetic energy to overcome the repulsive forces between them and fuse together on collision to form deuterons ($_1H^2$) and positrons (positive electrons):

$$_1H^1 + {}_1H^1 \rightarrow {}_1H^2 + {}_{+1}e^0$$

Deuterons then react with protons to form helium-3 and gamma radiation:

$$_1H^2 + {}_1H^1 \rightarrow {}_2He^3 + \gamma$$

Helium-3, however, does not react with protons under these circumstances. Instead, two helium-3 nuclei fuse together to form a helium-4 nucleus, liberating at the same time two protons which participate in further reactions (Figure 5):

$$_2He^3 + {}_2He^3 \rightarrow {}_2He^4 + 2{}_1H^1$$

The net reaction, the "burning" of hydrogen to form helium, is in terms of energy per unit mass the most productive of all nuclear processes and is the source of the energy of all stars for the greater part of their lives. It is estimated that the sun, after the lapse of 4.5 × 10^9 years, has used up about half its hydrogen.

When all the hydrogen in the core of a star has been burned, the core cools and once again contracts under the influence of gravitation when the temperature rises once more, reaching about 100 million degrees. What happens in a core of helium at this temperature? "We have come," says Fowler (*11*), "to the Gordian knot of the speculations on the building up of the elements. Two helium nuclei may combine to form a nucleus of mass 8, but as we have seen [CHEMISTRY, February 1964, page 11], any nucleus of mass 8 must be extremely unstable because none is found in nature. However, beryllium-8 *has* been produced momentarily in the laboratory and will certainly materialize in the hot and dense interior of a star. In fact, in that environment beryllium-8 will be produced as fast as it breaks down so that a small amount of it is always present. If so, an occasional beryllium-8 nucleus may, during its very brief lifetime, fuse with a helium-4 nucleus."

The net reaction is thus:

$$3\ {}_2He^4 \rightarrow {}_6C^{12} + \text{energy}.$$

As the temperature of the core of a star rises beyond about 2 × 10^8 °K., the velocity of the nuclei increases and this enables fusion reactions to take place between nuclei of greater charges by what is known as the "α" process. Thus, the successive fusion of α particles produces reactions like the following:

$$C^{12} + He^4 \rightarrow O^{16} + \text{energy}$$

$$O^{16} + He^4 \rightarrow Ne^{20} + \text{energy}$$

$$Ne^{20} + He^4 \rightarrow Mg^{24} + \text{energy}$$

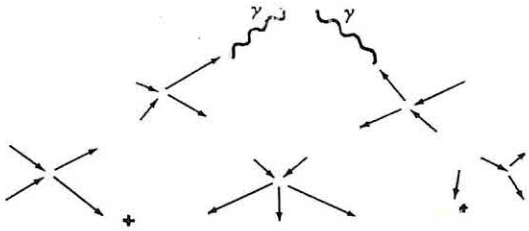


Figure 5. Hydrogen burning in stars yields helium and energy

All these fusion reactions are exothermic and are the source of energy radiated by stars. At still higher temperatures, the fusion process continues and produces such nuclei as Si^{28}, S^{32}, Ar^{36}, and Ca^{40}. The following reactions are also thought to occur under the same conditions:

$$C^{12} + O^{16} \rightarrow Mg^{24} + He^4 + \text{energy}$$

$$C^{12} + C^{12} \rightarrow Na^{23} + H^1 + \text{energy}$$

$$O^{16} + O^{16} \rightarrow P^{31} + H^1 + \text{energy}$$

$$O^{16} + O^{16} \rightarrow Si^{28} + He^4 + \text{energy}$$

Similar reactions involving the use of heavy bombarding particles have been studied in the laboratory. For example, ions of C^{13} have been accelerated in a cyclotron and used to synthesize element 102 (nobelium) from curium, but the reaction,

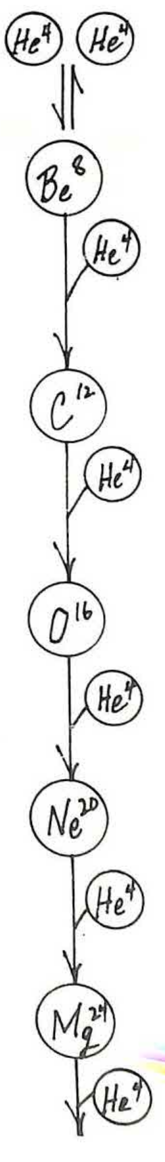
$$_{96}Cm^{244} + {}_6C^{13} \rightarrow 6\,n + {}_{102}No^{251}$$

appears to be more complicated than those just listed. Finally, as the temperature approaches the region 10^9 to 10^{10} °K., the core reaches thermonuclear equilibrium with large amounts of Fe^{56} present. Beyond iron and its neighboring nuclides the fusion process cannot go since these nuclides are the most stable of all. Up to this point, nuclear energy can be produced by fusion reactions; beyond it, only fission processes yield nuclear energy. The high cosmic abundance of iron is a reflection of its great nuclear stability.

Creation of the Heavy Elements

Some new mechanism must be invoked to account for the creation of elements beyond iron. Two main processes have been proposed, each based on the $n\ \gamma$ reaction. The first of these is catastrophic in character and is believed to take place in supernovae. For a brief

α - process



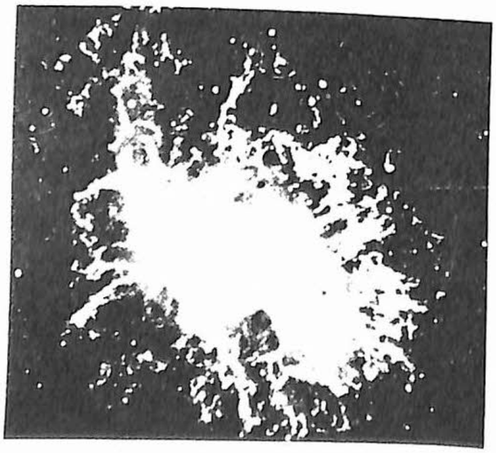
description of supernovae, I turn to the astronomer (*8*):

"A supernova at maximum light often becomes comparable in brightness to the total light emitted by its parent galaxy! Nothing is known with certainty about the cause of the supernovae explosions but it looks as though we have here the case of a star that is being blown up. The finest example of a supernova in our own Milky Way system (they come no more frequently than one in 300 years per single galaxy) is a star that was observed as a brilliant object by Chinese observers in 1054 A.D. and the after-effects of which can be seen today in the Crab Nebula in Taurus [Figure 6]. It was brighter at maximum than Sirius and since it was at the distance of the Crab Nebula —about 4000 light years—its intrinsic brightness at maximum must have been equal to the light of ten million of our suns."

r-process : rapid
s-process : slow

The *r*–Process. Supernovae explosions are, like those of megaton hydrogen bombs, accompanied by the release of neutrons though, of course, on a vastly greater scale. During the relatively short-lived blast of a supernova, these neutrons form elements up to bismuth. Heavier elements are produced from lighter elements, mainly iron, by successive neutron capture and subsequent β decay, just as Gamow visualized the process in his "big bang" theory. Neutron capture at a rate that is rapid compared with that of β decay, is called the rapid or *r*–process. The trend in this process is for an unstable nuclide, formed by neutron capture, to capture a second neutron before it can reach stability by decay. This process leads to the formation, in relative abundance, of Se, Br, Kr, Te, I, Xe, Cs, Os, Ir, Pt, Au, Th, and U.

Figure 6. The Crab Nebula. The gaseous remnant of a star that exploded in 1054 A. D.



Recent work has led to the belief that the transuranium element californium (Cf) is synthesized in some supernovae. Interestingly enough, californium has been detected in the debris of a hydrogen bomb explosion.

The *s*–Process. The second process by which elements heavier than iron can be created is by the capture of neutrons on a slow time scale. The source of the neutrons for this process is different from that for the *r*-process. Oxygen (O^{16}) present in the cores of stars known as red giants combines with a neutron to form O^{17}; Ne^{21} and C^{13} are formed in a similar manner. These three isotopes react with α particles to form unstable nuclei (the α n reaction) which liberate neutrons:

$${}_8O^{17} + {}_2He^4 \rightarrow {}_{10}Ne^{20} + n$$

The successive capture of these neutrons on a slow time scale leads to the formation in comparative abundance of such elements as Sr, Y, Zr, Ba, La, Ce, Pr, Nd, Pb, and Bi. The most exciting evidence of occurrence of the *s*-process is the recent spectroscopic detection of technetium (Tc), an unstable element of atomic number 43 whose most stable isotope has a half life of 2.1×10^5 years—far less than the age of the red giant stars in which it is found. The spectroscopic detection of this unstable element is one of the most convincing pieces of evidence that elements are being synthesized in stars.

According to current views, the sun cannot itself make elements heavier than helium though, of course, many heavier elements have been detected in the solar atmosphere. These must have been present in the interstellar medium from which the sun was formed. For this reason the sun is sometimes called a "second generation" star. The heavier elements in the sun include those believed to have been formed by the *r*–process in supernovae. Since the earth was presumably formed from the same interstellar medium as the sun, the elements present in its crust are also "the ash of a cosmic nuclear fire."

An interesting possibility has recently been discussed (2): "Another solar system might have condensed out of material consisting mainly of hydrogen, and gas ejected from stars which had gone through hydrogen burning, helium burning, the *s*–process, the α–process and the *e*–process (another process for making iron group elements) but not the *r*–process. In this case, among the heavy elements the *s*–process isotopes would be present but the *r*–process isotopes would be absent, so that elements which are predominantly built by the *r*–process would be in very low abundance. Thus, in such a solar system, the inhabitants would have a very different sense of values, since they would have almost no gold and . . . no uranium."

Evidently, the evolution of the elements, like that of the stars, is quite a complicated process. Indeed, the two are closely related. During the evolution of stars, the changing conditions at their centers, where temperatures range from a few million to tens of thousands of millions of degrees and pressures vary by factors of a million or more, provide the wide variety of conditions needed for the many different kinds of nuclear processes that are believed to be involved in the formation of the elements.

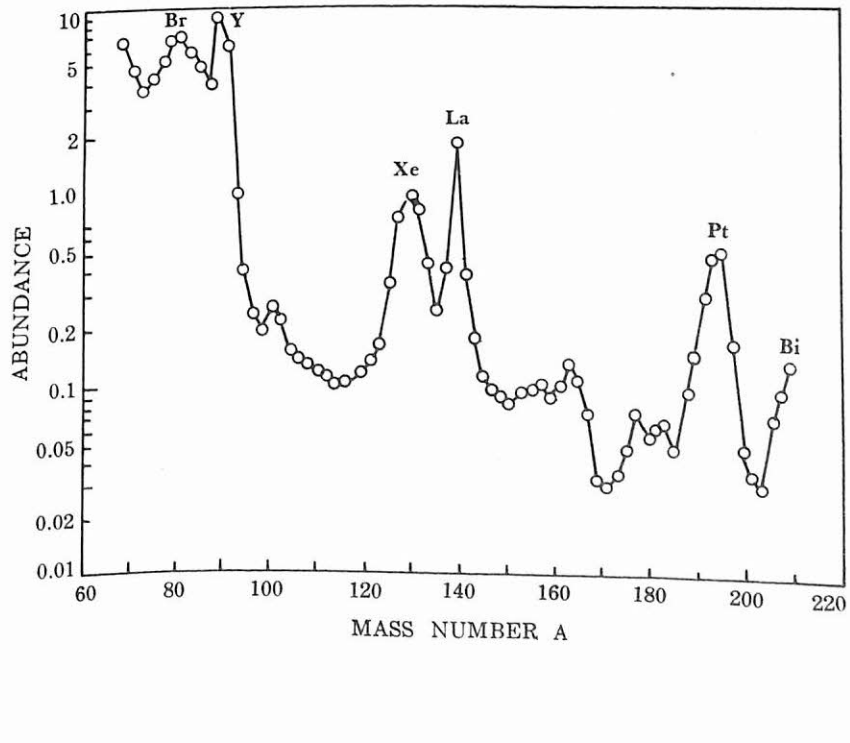
Abundance of Elements and Nuclear Structure

As already stated, any satisfactory theory of the origin of the elements must be able to account for their relative abundances in the universe. It is reasonable to expect some correlation between the cosmic abundances of the elements and the properties of the nuclei—for example, nuclear stability and the processes by which the elements were formed. The correlation is likely to be more clear-cut if it is sought, not for the elements themselves, but for particular nuclear species (nuclides).

Since the isotopic constitution of the elements is known from the results of mass spectrometry, it is a simple matter to convert a table of cosmic elemental abundances to a table of cosmic nuclide abundances, each nuclide being characterized by its mass number. To do this, however, one must make an important assumption—that the isotopic constitution of the elements is constant throughout the universe. This may not be true. It is conceivable that a nuclide may be formed by different processes and that in different parts of the universe, the relative importance of these processes may vary. However, the assumption of constant isotopic ratios is substantially true for meteoritic matter and for the earth's crust and hence for the solar system. More than that we do not know with certainty. In Figure 7, the abundances of the nuclides of odd mass

Figure 7. Abundances of elements (A > 70) plotted as a function of the mass number A

This graph shows odd-A nuclides only. The abundance curve of even-A nuclides shows the same peaks. Abundances of the elements are given relative to a value of 10^6 for the abundance of silicon. [Reproduced from *Physical Review*, **121**, 1389 (1960) with the permission of the publishers]



number are plotted against their mass number. There are periodicities in the abundances with peaks at Br, Xe, and Pt and at Y, La, and Bi.

The curve of Figure 7 stands in striking contrast to the one shown in Figure 3 (Part 1) where abundance was plotted against atomic number Z.

Some years ago, it was noticed that the abundance of nuclides containing certain numbers of neutrons or protons is unusually high. These numbers—2,8,20,28,50,82,126—were at first known as "magic" numbers because their basis was purely empirical. They are now well understood in terms of a quantum mechanical shell model of the nucleus. Experiment shows that nuclides with closed shells of protons (or neutrons) have a markedly smaller cross section for the capture of neutrons compared with that of other nuclides with mass numbers in the same region. When nuclides are formed by successive neutron capture, those with closed shells should be more abundant than their immediate neighbors in the mass number series.

Neutron cross section; ability to capture neutrons

The peaks in the abundance curve shown in Figure 7 have been ascribed to magic number effects. For example, Coryell (*10*) suggests that the peaks at Br, Xe, and Pt are a consequence of the *r*-process pile-up in fast neutron capture on a fast time scale, of primary antecedent species with neutron numbers 50, 82, and 126. This would be expected only if a blast of fast neutrons rather suddenly died out leaving the cosmic material to undergo β decay to the valley of stability without further serious perturbation.

The peak in the abundance curve at Fe^{56} (not shown in Figure 7) is related to the high stability of this nuclide and to the fact that its production marks the culmination of nuclear fusion processes. The high abundance of α-particle nuclei such as O^{16}, Ne^{20}, Mg^{24}, Si^{28} . . . Ca^{40}, etc., is a consequence of their high stability and also of the great abundance in the universe of helium from which they are formed.

The theory of the stellar origin of elements provides an explanation of other features of the abundance curve but it has not, of course, been wholly successful—for example, in explaining the abundances of some of the lightest and some of the heaviest elements. The cosmic rarity of deuterium, lithium, beryllium, and boron is a consequence of the relative fragility of their nuclei. They cannot survive under the conditions in which helium is synthesized from hydrogen. But how these elements are synthesized in stars is one of the unsolved problems of cosmochemistry. At the other end of the scale, the extremely low abundances of mercury, lead, thallium, and bismuth cannot be explained on the basis of existing theory of nucleosynthesis.

As so often happens in opening new fields of knowledge, there is constant interplay between theory and observation; improvements in the accuracy of abundance data lead to modifications of theories of nucleosynthesis; these in their turn may lead to suggestions that some abundance data are inaccurate and in need of revision. Although much has already been achieved in understanding the origin of the elements, much still remains to be done.

A striking contrast may be drawn between evolution on the earth, and the evolutionary processes in stars. Evolution of molecules and the consequent evolution of living organisms is closely related to the chemical properties of atoms—to the number and configuration of their outer electrons. The driving forces in evolution of the elements and stars, on the other hand, have their origin in the innermost recesses of atoms—in their nuclei.

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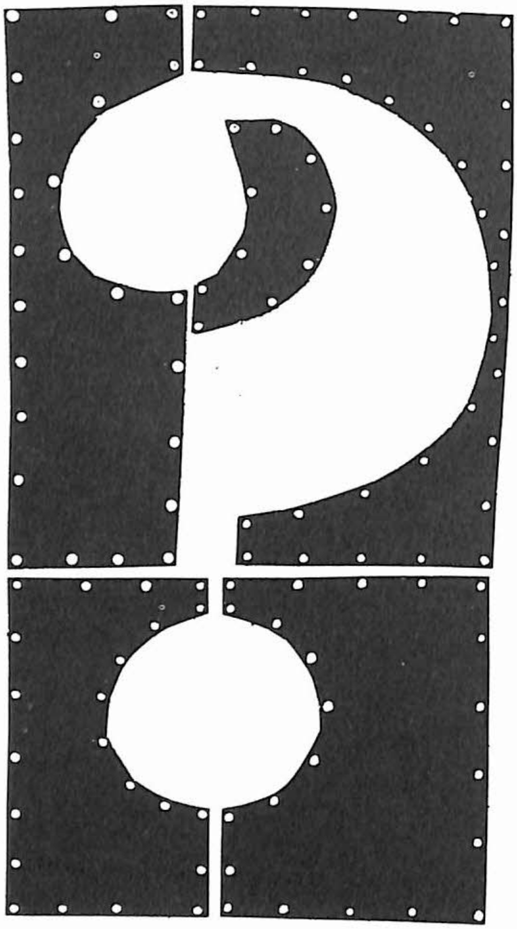
WHAT IS A METAL



Frank H. Verhoek, *The Ohio State University, Columbus, Ohio*

Of the 90-odd elements which occur naturally, about 70 are classified as metals. High school chemistry courses usually include a discussion of the properties of compounds of the metals, but little attention is paid to the metals themselves. Our habit of writing the equation for the reaction of sodium with chlorine as

$$2Na + Cl_2 \rightarrow 2Na^+Cl^-$$

makes it appear as though the element sodium came to the experimenter as a collection of separate atoms. Actually, of course, it exists in the solid state as an elemental compound of sodium atoms with other sodium atoms, and in the reaction under discussion a sodium atom must be separated from other sodium atoms in an expenditure of energy which is nearly the same as that required to produce a chlorine atom from the chlorine molecule.

Properties of Metals

—Malleability and ductility: they can be pounded into sheets and drawn into wires

—High tensile strength: they do not separate easily into pieces when the ends are pulled

—Opacity: except in extremely thin layers, light will not pass through

—Metallic lustre: they reflect light of all wave lengths

—Good electrical conductivity: they conduct well in the solid and when melted; conductivity decreases as the temperature is raised

—Good heat conductivity: they conduct heat in the solid and when melted

—Metals when melted remain liquid over a long temperature range before the boiling point is reached

—Metals can react with nonmetals and form positive ions when they do

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Only the last of these is strictly a chemical property. The others are physical properties, and emphasize again the fact that the properties we recognize as metallic properties are not characteristic of *atoms*, but rather are characteristic of a *state of aggregation* of certain types of atoms. How can these properties be interpreted in terms of the nature of the binding which holds metal atoms to each other?

Electrons in Metals

Perhaps the most unusual of the properties listed, and the one which most distinguishes a metal from other substances, is the easy conduction of electricity (Table I). Chemists believe that this conductivity arises from the ease with which electrons can move through metals: The current which flows through a wire is the result of the passage of electrons along the wire. No chemical change accompanies this passage, nor does reaction occur at the points where charge enters and leaves the wire.

This behavior is opposite to that observed in electrolysis processes, where ions are formed or neutralized at the electrode surfaces. Further, in electrolysis processes or in conduction in gases, current will not flow until a minimum voltage is reached. For current to flow in a wire, on the other hand, no minimum voltage is required, and the current is directly proportional

TABLE I. ELECTRICAL RESISTIVITY[a]

	Ohm-Cm.		Ohm-Cm.
Lithium	8.6×10^{-6}	Glass	1×10^{10}
Carbon (graphite)	1.38×10^{-3}	Porcelain	1×10^{12}
		Sulfur	4×10^{16}
Sodium	4.4×10^{-6}	Calcium fluoride	8×10^{17}
Magnesium	4.4×10^{-6}		
Aluminum	2.6×10^{-6}	Sodium chloride	5×10^{16}
Potassium	6.6×10^{-6}		
Iron	9.8×10^{-6}	Acetone	5×10^{5}
Cobalt	6.3×10^{-6}	Alcohol	1.7×10^{5}
Nickel	6.9×10^{-6}	Benzene	1.3×10^{5}
Copper	1.6×10^{-6}	Water	2.5×10^{5}
Zinc	5.9×10^{-6}		
Rubidium	12.5×10^{-6}		
Silver	1.6×10^{-6}		
Tin	11.5×10^{-6}		
Antimony	39×10^{-6}		
Cesium	19×10^{-6}		
Gold	2.4×10^{-6}		
Lead	21×10^{-6}		
Bismuth	110×10^{-6}		

[a] The electrical resistivity is equal to the resistance in ohms of a block of material 1 square cm. in area and 1 cm. thick. The scientific notation is used in the table. For comparison with decimal notation, the resistivity of lithium is 0.0000086 ohm-cm.; that of graphite is 0.00138 ohm-cm. The smaller the value of the resistivity, the better the material is as an electrical conductor.

to the voltage [Ohm's law $I = (1/R) \times E$]. We conclude, therefore, that current flow in metals does not result from ionization processes: There must already be present in the metal of the wire electrons which are not attached to specific atoms, which can be exchanged for fresh electrons from a battery, and which are free to travel through the wire.

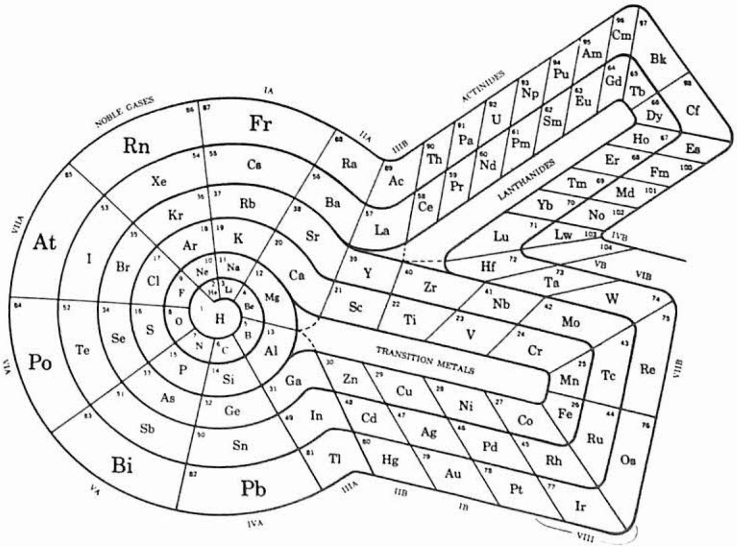
The freedom with which electrons move in metals was dramatically illustrated in experiments in which a potential difference was detected between two ends of a wire wound on the rim of a wheel spun at high speed and suddenly stopped. The inertia of the electrons was just that to be expected of particles carrying the electronic charge and having the known weight of the electron, as determined from experiments with cathode rays [Tolman R. C., Stewart, T. D., *Phys. Rev.* **8,** 97 (1916); **9,** 164 (1917). Tolman, R. C., Karrer, S., Guernsey, E. W., *Ibid.*, **21,** 525 (1923)].

Electron Structure of Metal Atoms. On the basis of conductivity data, we conclude that the electrons in metals are free to move. On the other hand, the high tensile strength of metals indicates that the metal atoms are bound together by forces of appreciable magnitude. How can we reconcile the freedom of electrons to move with the strength of the bonding between atoms? Our experience with bonds in covalent compounds, or between the carbon atoms within a crystal of diamond, would lead us to conclude that strong bonding is associated with electrons tightly bound in shared pairs, and no conductivity.

In order to answer the question let us first examine the electron structure of the metal atoms. From their positions in the periodic table (Figure 1), it is evident that the metals are those elements which have relatively few electrons in their valence shells. Atoms of *representative metals* in groups I and II have only one or two, and *transition metals* have two electrons (occasionally one) in the outermost shell overlaying *d*-electrons of the shell of the next lower principal quantum number. Having so few available electrons, the metal atoms cannot combine with each other to produce the eight-in-the-outer-shell configuration of a noble gas. There are just not enough electrons to bind two atoms together in ordinary covalent or electrovalent bonds, either by sharing in pairs, or by transfer to form positive and negative ions.

Community Sharing. An approach to the stability of the eight-in-the-outer-shell configuration can be made, however, if we assume that electrons can be shared among more than two atoms. This is the essential feature of the binding in metals, and the sharing is really on a grand scale. Each atom in a metal crystal contributes all of its valence electrons to the community, retaining only an extremely small share in them, but at the same time acquiring a small share of the valence electrons of all the other atoms. The result of this community sharing has been likened to a group of positive ions (the metal atoms without their valence

Figure 1. The periodic table showing the positions of metals (shaded) and nonmetals



electrons) in a "sea" of electrons, but this does not quite call up the right picture, because one tends to think of the ions as floating aimlessly in this sea. This is not correct: The ions occupy definite positions at measurable distances from each other in a *crystal lattice* (Figure 2). The valence electrons, however, are not attached to any individual ions or pair of ions; they belong to the crystal as a whole, and are free to move about from place to place. Even though the electrons are free to move, the accumulation of negative charge between the positive ions serves to act as an effective binding force and the energy required to separate metal atoms from each other is not appreciably different from that required to separate other atoms from each other (Table II).

Properties of Metals

The theoretical picture of a solid metal which emerges is that of a group of positive ions, arranged within the metal crystal at definite positions in a crystal lattice, surrounded and bathed in electrons which are free to move, and which, at the same time, provide an environment of negative charge which binds the ions together. If this model is any good, it should enable us to interpret the properties of metals in terms of it, and perhaps to predict some properties which are not listed on page 6.

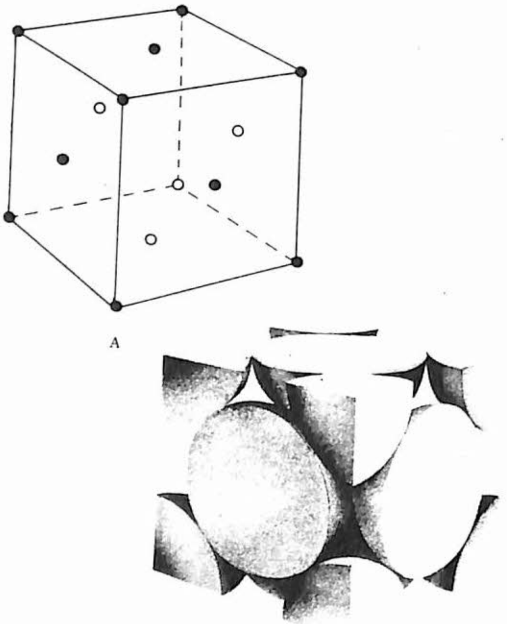


Figure 2. Ion positions in a *face-centered cubic* lattice, one of the three common crystal lattices found in metals. In *A*, positions of the nuclei are marked as solid circles (visible on exposed surfaces of the imagined cube) and open circles (not visible from the viewpoint of the observer). In *B*, units in the lattice are assumed to be spheres in contact with each other

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Electrical Conductivity. Freedom of electrons to move permits current to be carried when a potential difference is applied. Free existence of the electrons within the metal prior to the application of the potential difference means that no chemical reactions nor ionization processes are needed to cause current to flow, distinguishing metal conduction from electrolysis or conduction in gases. Moving electrons, however, may be expected to collide with things in their path. In a well ordered crystal lattice, the positive ions are neatly arranged in their specified positions, and the electrons can move easily among them. Anything which distorts the lattice will tend to put obstacles in the way of the moving electrons. This is what happens when metals are heated. The metallic ions in the lattice acquire energy, and begin to vibrate around their proper positions, causing them to interfere with the easy movement of the electrons. Sometimes this interference is spoken of as a collision between the electrons and the out-of-position ions, but this does not call forth a correct picture. Rather, the interference results from interaction of the charge on the electron with the irregularity of the electric field within the crystal, since the field is altered by the motion of the ions. The result of this interference is that the electrons move through the lattice with more difficulty at higher temperatures, which we observe as an increase in the resistance of the metal at higher temperatures.

A similar increase in resistance is caused by any other process which distorts the regularity of the electric field of the ions. Such distortion could arise from the introduction of "foreign" atoms or ions, whose electrical characteristics are different from those of the atoms of the parent metal, and it is found experimentally that the resistance of alloys, or of impure metals generally, is higher than that of the pure metal (Table III). Similarly, mechanical working of the metal, by bending, stretching, or pounding, which changes the positions of the ions with respect to their perfect order, will cause an increase in resistance.

The resistance due to impurities or to distortion produced by mechanical working will not be expected to change with temperature, whereas vibration of the atoms due to heat motion will subside at lower temperatures. Hence the resistance at low temperatures is predominantly that of the imperfections, for which the number and type will depend upon the previous history of the sample, and the residual resistance at low temperatures will vary from sample to sample, as observed.

A certain amount of heat disorder exists at any temperature, so that when a current passes, some collisions of electrons with ions occur. The number of collisions per unit time, and their violence, will be greater, the greater the current passing. These collisions will transfer energy to the ions, producing a random vibration of them which will appear as heat. This is the explanation of the heating effect of an electric current, measured as I^2R.

TABLE II. HEAT OF ATOMIZATION OF SOLIDS[a]

Metals		Nonmetals	
Lithium	37.07	Carbon (graphite)	171.698
Sodium	25.98	Silicon	88.04
Magnesium	35.9	Phosphorus	75.18
Aluminum	75.0	Sulfur	53.25
Potassium	21.51	Iodine	25.482
Calcium	46.04		
Iron	96.68	Covalent compounds	
Cobalt	105	Ammonia	65
Nickel	101.61	Carbon monoxide	129
Copper	81.52	Carbon dioxide	130
Zinc	31.19	Methane	80
Cesium	18.83	Hydrogen chloride	54
Tungsten	201.6	Water	78
Gold	82.29		
Lead	46.34		
		Alloys	
Electrovalent compounds		AlCo	106
LiCl	81.89	Cu_2Zn_3	54.5
NaCl	76.61	Mg_2Sn	54.0
KCl	77.35	$MgZn_2$	37

[a] The heat of atomization is the energy needed to produce separated gaseous atoms from solid elements or compounds. The values are in kilocalories per mole of gaseous atoms at 298 °K. Those given for compounds which are not solid at 298 °K. are approximate.

TABLE III. ELECTRICAL RESISTIVITY OF ALLOYS

	Ohm-Cm.
Brass (66% Cu, 34% Zn)	6.3×10^{-6}
Bronze (88% Cu, 12% Sn)	18×10^{-6}
Constantan (60% Cu, 40% Ni)	49×10^{-6}
German silver (60% Cu, 25% Zn, 14% Ni, 0.3% Fe)	30×10^{-6}

TABLE IV. THERMAL CONDUCTIVITY[a]

Lithium	0.167	Cement	0.00048
Carbon (graphite)	0.038	Glass	0.0025
Sodium	0.323	Marble	0.0059
Magnesium	0.370	Porcelain	0.0025
Aluminum	0.485	Calcium fluoride	0.0239
Potassium	0.237	Silver chloride	0.0026
Iron	0.148	Sodium chloride	0.0166
Cobalt	0.165	Acetone	0.00043
Nickel	0.140	Alcohol	0.00044
Copper	0.927	Benzene	0.00041
Zinc	0.270	Water	0.00140
Silver	1.000		
Gold	0.707		

[a] The units are calories passing each second through a block of material for which the area is 1 square cm. and thickness 1 cm. when the temperature difference across the thickness is 1 °C. The higher the value the better the conduction of heat.

Heat Conductivity. The high conductivity for heat (Table IV) is similarly explained by the moving electrons. In a nonmetallic solid the vibratory motion of the atoms at the hot end of the substance can only be transferred to the neighboring "cooler" atoms as a result of the alternate increase and decrease of the forces acting on the neighbors as the "hot" atoms sway back and forth. In metals, however, the electrons can pick up energy from a collision with the "hot" atom and give it up again to a cooler atom which may be many neighbors away. The mobility of the electrons, therefore, provides a method of energy transfer not available to nonmetallic substances, and the thermal conductivity is correspondingly increased.

Metallic Luster and Opacity. The luster of metals is the result of the fact that light of all visible wave lengths is strongly reflected by the metal. When light falls upon a flat surface, it may be reflected, transmitted, or absorbed, and all the energy of the incident light must be accounted for in the sum of the energies in the reflected beam and the transmitted beam and the energy stored in the substance by absorption. If no light is transmitted, as in the case of metals, all the energy must be accounted for by reflection or absorption. The small amount of absorption which does take place in metals occurs in the first few hundred atom layers at the surface; the remainder of the light is reflected. Except for copper and gold, the reflectivity is high for all wave lengths in the visible spectrum, so that white light, falling on a metal, gives the white, shiny appearance which we call metallic luster. The equations of the electromagnetic theory of light show that this high reflectivity is predicted if electrons in the metal are free and not bound to particular positions; hence this property is further evidence for the correctness of the picture of metallic binding.

Malleability and Ductility; Tensile Strength. The properties of being malleable and ductile are related to the tensile strength, because they depend upon the ease with which metals are deformed without loss of cohesion between particles. As one part of the metal moves with respect to another part there is still a strong attraction between the two portions. Movement cannot occur easily in any arbitrary direction, but is constrained to occur along certain "slip planes," dictated by the packing of the atoms or

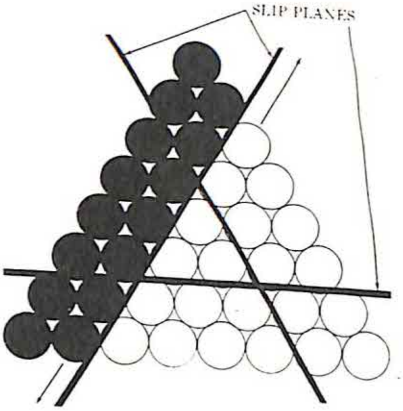

Figure 3. Slip planes in a metal crystal

ions in the crystal (Figure 3). All the ions above the slip plane do not move simultaneously, but a "dislocation" moves step-by-step across the crystal. The dislocation in Figure 4 is shown as though it had been introduced into an originally perfect crystal lattice. Often, however, the crystal is originally imperfect, showing dislocations or *vacancies* as in Figure 5, and the effect of applying stress is to force movement along the slip planes containing the dislocations.

The deformation is accomplished by the gliding of one plane of ions over another, so that the ions in the layers never separate appreciably from one another. In the model of metals which we have been discussing, therefore, the ions remain bathed in the sea of electrons in a manner during slip which is almost the same as their condition when no deformation is taking place. The binding energy of the crystal is little disturbed during the deformation, and after the deformation is complete, the final condition of the ions is the same as the beginning, except for those at the extreme front and rear edges of the slip planes, where a separation of ions has indeed occurred. The condition of the metal near the dislocation during deformation can be looked upon as a localized melting (see below), and the energies involved are of a similar magnitude. The similarity of the structure before, during, and after slip accounts for the fact that strong binding between the ions is maintained when the metal is worked; thus the solid does not shatter when pounded or pulled, as a nonmetallic substance does.

Molten Metals. Metals retain their properties of high conductivity for electricity and heat, and their metallic luster, when melted. This is understandable in terms of the model if we assume that in the melt, too, the valence electrons are given to the community to be shared among all ions. The regularity of the crystal lattice, however, will have been grossly disturbed, so that there should be much more interference with the passage of electrons among the ions, with a corresponding decrease in the electrical conductivity. Antimony and bismuth are anomalous in this respect (Table V). The binding forces within the melt, however, are still maintained at a high fraction of their full strength, since the ions are still close together and bathed in the

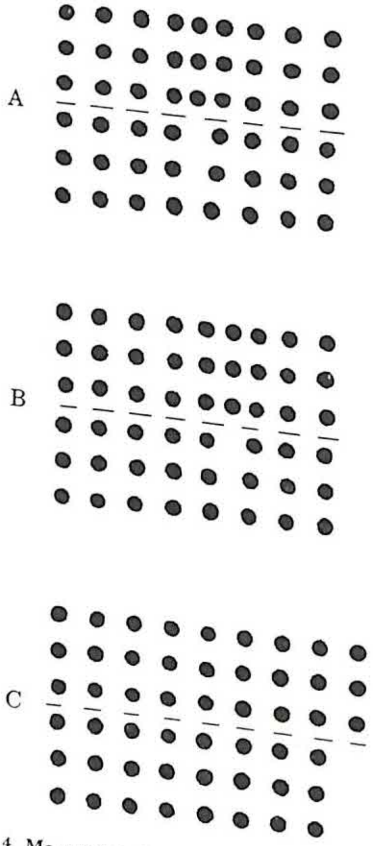

Figure 4. Movement of a dislocation. *A*, a dislocation in the form of an extra row of atoms appears above the slip plane. Note expanded distance between the atoms below the plane. *B*, the dislocation has moved one atomic distance to the right. *C*, after the dislocation has moved to the crystal edge

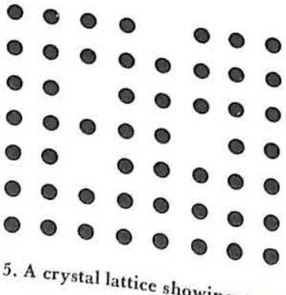

Figure 5. A crystal lattice showing vacancies

TABLE V. RATIO OF THE RESISTIVITY OF A MOLTEN METAL TO THE RESISTIVITY OF THE SOLID METAL AT THE MELTING POINT[a]

Lithium	1.68	Silver	1.9
Sodium	1.44	Cadmium	1.89
Magnesium	1.63	Indium	2.12
Aluminum	1.65	Tin	2.1
Potassium	1.53	Antimony	0.70
Iron	1.09	Cesium	1.65
Copper	2.07	Gold	2.28
Zinc	2.09	Lead	2.06
Rubidium	1.61	Bismuth	0.43

[a] The higher the resistivity ratio, the greater is the loss of electrical conductivity when the solid material is melted.

electron sea; hence, once melted, a great deal more energy must be added actually to separate atoms from each other. Thus the boiling of a metal, which produces this separation, will occur only at much higher temperatures, and we observe the long liquid range characteristic of metals.

Commercial Metals

Properties of metals have been discussed above as if metals were physically homogeneous and the same throughout except for occasional dislocations. A commercial metal, even of the purest, is rarely this uniform, since it will be made of an agglomeration of many crystals (Figure 6). Some of the properties, therefore, depend upon how these crystals fit together. In conduction, electrons and energy must be transmitted across the boundaries between one crystal and another. The magnitude of these interposed barriers will depend upon the previous history of the metal, since the way in which the metal has been formed and worked will determine the size and alignment of the crystals. Annealing—heating the metal for varying periods of time to temperatures below the melting point—permits ions or atoms in less stable positions to migrate to more stable positions, changing the size of the crystals and the orientation of grain boundaries, as well as evening out dislocations within individual crystals. Elaborate recipes for heat treatment of metals are therefore valuable in preparing commercial samples of metals having particular properties. With alloys these heat treatment procedures are of even more importance, since the distribution and chemical reactions of the alloying substances can be changed by changing the temperature, and then the final state "frozen" by a quick chilling or *tempering*.

Defects of the Model

A major wrong prediction of the above theory is that the electrons, if free, should make an appreciable contribution to the specific heat of the metal, since they should be able, by acquiring a greater velocity of motion, to absorb energy when the metal is heated. The specific heat of a metal, however, is almost entirely accounted for by the increase in vibratory motion of the atom kernels on heating. This defect can be accounted for by applying the concepts of quantum mechanics to the model of metals. The application leads to a model in which the electrons lie in specific energy levels, with not more than two in a level (Pauli Exclusion Principle). Only when it is near in energy to a level which has less than two can an electron accept a small amount of energy to raise it to a higher unfilled level. All electrons in filled levels far lower in energy than the unfilled levels cannot accept the small amounts of energy offered to the metal on heating, since these amounts would be insufficient to raise the electrons to an unfilled level; hence the electrons in low energy levels cannot contribute to the specific heat. A further conclusion from the quantum mechanical model is that the energy levels are grouped in bands of energy with gaps between. If all the levels in a band are filled with two electrons each, conduction is possible only by giving an electron sufficient energy to lift it past the gap to an unfilled level in the band of next higher energy. These concepts are particularly important in dealing with the semiconductors from which solid-state transistors are made, but the picture of free electrons is sufficient for a qualitative explanation of most of the properties of metals.

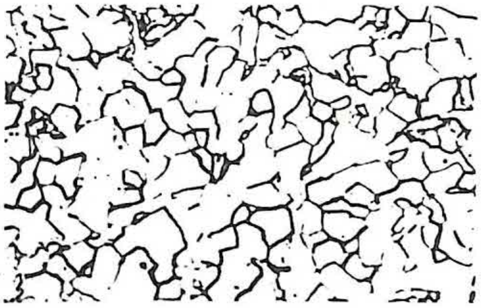

Figure 6. Etched surface of low carbon steel magnified 300 times showing boundaries between crystal grains

Courtesy Republic Steel Corp., Research Center

FRANK H. VERHOEK, professor of chemistry at Ohio State University, received a Ph.D. from the University of Wisconsin in 1933 and a D.Phil. in 1935 from Oxford University. He has been a consultant for Argonne National Laboratory, U. S. Naval Ordnance Test Station, and Battelle Memorial Institute, and author or coauthor of text books and more than 40 papers in scientific journals.

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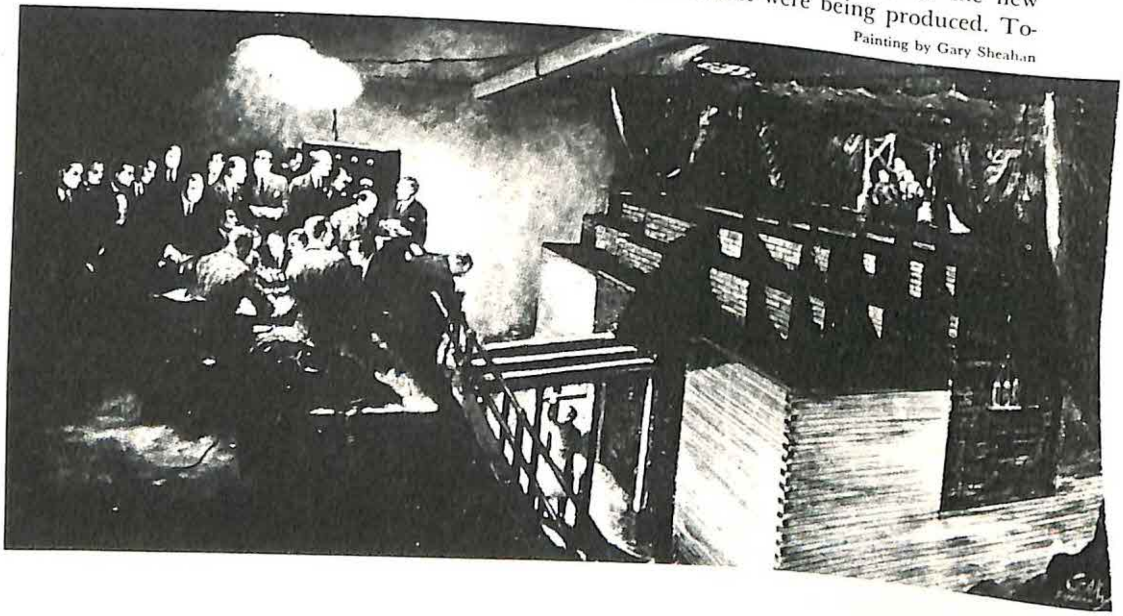
PLUTONIUM, the ornery element

Glenn T. Seaborg, *Chairman, U.S. Atomic Energy Commission*

Realization of the alchemist's dream of large-scale transmutation and announced to the world with an exploding bomb, plutonium in peacetime promises to provide a phoenixlike fuel

The story of plutonium is one of the most dramatic in the history of science. For many reasons this unusual element holds a unique position among the chemical elements. It is the first realization of the alchemist's dream of large-scale transmutation, the first synthetic element to be seen by man, and one of its isotopes has special nuclear properties which give it overwhelming importance in human affairs. No other fundamental scientific discovery has exploded in man's face as this one did: The first announcement of its existence was the bomb dropped over Nagasaki.

No other element has been so dramatic in its quantitative growth. Plutonium was first identified at Berkeley, Calif., late in 1940 and early in 1941, through experiments involving tracer amounts, picograms (10^{-12} gram) or less. Two years later, the microgram stage was reached with the first weighable quantity of plutonium. There followed experiments with milligram and gram quantities needed to perfect the chemical processes now employed at Hanford and Los Alamos. Less than three short years after the first weighable quantity was obtained, kilogram amounts of the new man-made element were being produced. To-



Painting by Gary Sheahan

day, for commercial fabrication of plutonium into fuel elements for power reactors, we talk about tons of plutonium. Thus, the scaling-up from discovery to the present status is by a factor of more than 10^{18}—an increase of more than a billion billion times.

Its Eccentricity Is Almost Unbelievable

It is only natural that an element so unusual, and in some respects so difficult and unpleasant as plutonium, should have its critics. Dr. Robert E. Wilson, Commissioner of the AEC, has said some rather harsh things: "If there ever was an element which deserved a name associated with hell," he says, "it is plutonium. This is not only because of its use in atomic bombs, which certainly would amply qualify it, but also because of its fiendishly toxic properties, even in small amounts." He mentioned other troublesome characteristics including the wide variation in the value of its more important isotopes, ranging from $450,000 per pound for plutonium-238 to a few dollars a pound for plutonium-240.

I cannot quarrel with the accuracy of the charges against plutonium. In fact I can elaborate plutonium's claim to being at the same time so ornery and so unusual as to approach the unbelievable. Under some conditions, plutonium metal can be nearly as hard and brittle as glass, under others as soft and plastic as lead. It burns and crumbles quickly to powder when heated in air, or slowly disintegrates when kept at room temperature. Pure plutonium metal undergoes no less than five phase transitions between room temperature and its melting point. The metal thus has six allotropic modifications.

Plutonium has remarkable characteristics in its several phases. Except for one part of the temperature range of the alpha phase, there is not one of the phases for which both the coefficient of thermal expansion and the coefficient of electrical resistivity have the conventional sign. Strange indeed is the fact that in two of its phases, delta and delta prime, plutonium actually contracts as it is being heated. Recently we have found to our surprise that the pure metal in its alpha, or brittle, phase can under certain conditions be rolled to a very thin foil about 0.001 cm. thick.

Its chemical properties are no less unusual. Plutonium has four oxidation states that can exist together in aqueous acidic solution in equilibrium with each other at appreciable concentrations. This situation is unique among all of the chemical elements. And, of course, plutonium occupies a totally unexpected and unpredicted position in the periodic table of the elements.

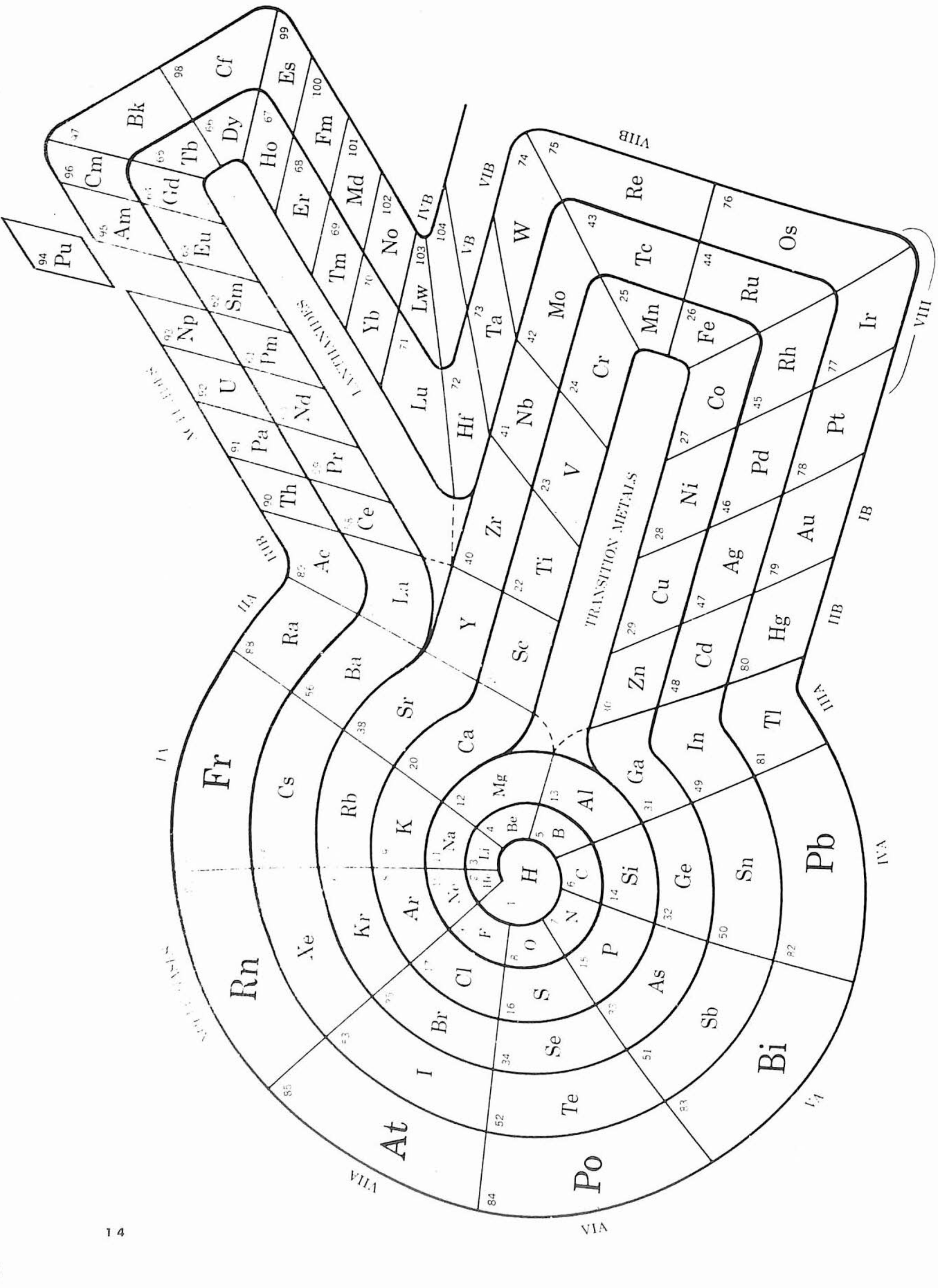
The atoms of plutonium-239 change continuously to those of a completely different element but so slowly that after thousands of years no more than 10% would be changed. Yet the change is so rapid that the heat generated by the reactions would cause the material to feel warm to your hand. Because of this self-heating property, new experimental techniques for thermal expansion and thermodynamic studies had to be devised. Finally, I must say that Dr. Wilson's indictment of its poisonous quality is almost an understatement. A particle the size of an ordinary speck of dust, about 0.6 microgram, constitutes the maximum amount that can be accumulated in an adult person without eventually causing significant body damage.

Early History

Perhaps I am so well acquainted with plutonium's early childhood that I view it as one might a bad child—difficult and even exasperating in its conduct at times but replete with fascinating possibilities. In the case of plutonium, these possibilities have a vital significance for the future of nuclear technology. Also plutonium occupies a significant place in my own life. I remember our wartime quests for plutonium in amounts large enough for military use as an epic rivaling the legendary adventures of Paul Bunyan. It is a tale of

A historic moment. At 3:25 P.M. on December 2, 1942, beneath the stands of Stagg Field at the University of Chicago, a team of scientists led by the late Enrico Fermi brought under man's control the formidable power of the atom; that is, criticality (self-sustained chain reaction) of the nuclear reactor was achieved.

Fermi is standing next to the instrument rack near the balcony rail with a slide rule in hand computing the rise of neutron count in the reactor. At his left is Walter H. Zinn leaning on the balcony rail with papers in his hand. Behind Fermi is H. Compton (with mustache), director of the operation. Twenty-six members of the team are shown, but the total number is believed to have been 45 to 50. The one woman physicist, Leona Woods Marshall, is seated at the table


TRANSITION METALS
LANTHANIDES
IA
IIA
IIIB
IVB
VB
VIB
VIIB
VIII
IB
IIB
IIIA
IVA
VA
VIA
VIIA
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
F
Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
Ar
K
20 Ca
Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
Zn
Ga
32 Ge
As
34 Se
Br
Kr
Rb
38 Sr
Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
Xe
Cs
56 Ba
La
Ce
Pr
Nd
Pm
62 Sm
Eu
Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
Yb
71 Lu
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
Rn
Fr
88 Ra
Ac
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lw
104

14

prodigious contrasts, the disparities between working out processes using barely weighable quantities of the new element and projecting these microscopic amounts into the Gargantuan scale of production reactors and chemical processing plants.

I was one of those young chemists profoundly stirred by the experiments performed by Fermi, Segré, and their coworkers when they began to bombard uranium with neutrons and found several beta emitters as products of these neutron reactions. During the fall of 1934, we began to get articles about this work from Rome in an Italian journal, and we tried to decipher them. The excitement was spreading in many places. Several groups were interested in these beta radioactive isotopes produced. Hahn and Meitner and later Hahn, Meitner and Strassman in Germany studied the beta emitters for a number of years, assuming they were transuranium isotopes.

As a graduate student I chose transuranium elements as my topic for a seminar and gave an hour-long talk on these elements. Like everyone else, I believed entirely that these beta radioactivities were transuranium isotopes and considered myself a minor expert on the so-called transuranium elements.

History shows that we were wrong. An involved and complex detective story unfolded in which a number of eminent sleuths were engaged over a number of years. At last the true transuranium elements were unveiled and their false forerunners exposed as the fission products they were. Ironically, those studying the fission process then found the transuranium elements. From this, it can be seen how plutonium, belonging to this unpredictable transuranium group, would start off on the wrong foot.

The early work on plutonium was carried on in secrecy, because of its potential military application. Throughout 1941, plutonium was referred to by the code name of copper, which was satisfactory until it was necessary to introduce the element copper into some of the experiments. This posed the problem of distinguishing between the two. For a while then, plutonium was referred to as copper and the real copper as honest-to-God copper. But this grew too cumbersome and finally we were forced to give the new element its present name.

Because the first man-made element had already been christened neptunium after the planet Neptune, we followed this pattern by naming the next element plutonium, Pluto being the second and last known planet of our solar system beyond Uranus. We debated whether the name should be plutium or plutonium and chose the latter because it sounded better. There was also the matter of a symbol and again propriety was overruled. Rather than the more proper Pl, we chose Pu for the reason you would suppose. Experience with the ornery element has proved our choice of Pu to be most descriptive.

In translating from microgram amounts of plutonium to milligrams and grams and at last to kilograms, ultramicrochemistry came into its own during those hectic days. Even so, there were moments of comic relief as when

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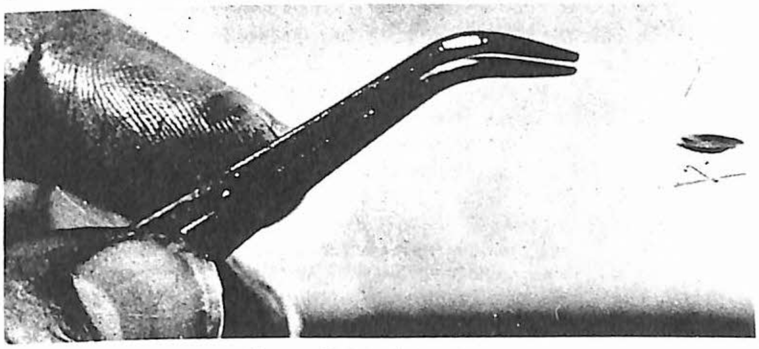
$_{92}U^{238} + {}_{0}n^{1} \rightarrow \gamma + {}_{92}U^{239}$ (Instantaneous)

$_{92}U^{239} \rightarrow {}_{-1}\beta^{0} + {}_{93}Np^{239}$ (Half life 23 minutes)

$_{93}Np^{239} \rightarrow {}_{-1}\beta^{0} + {}_{94}Pu^{239}$ (Half life 2.3 days)

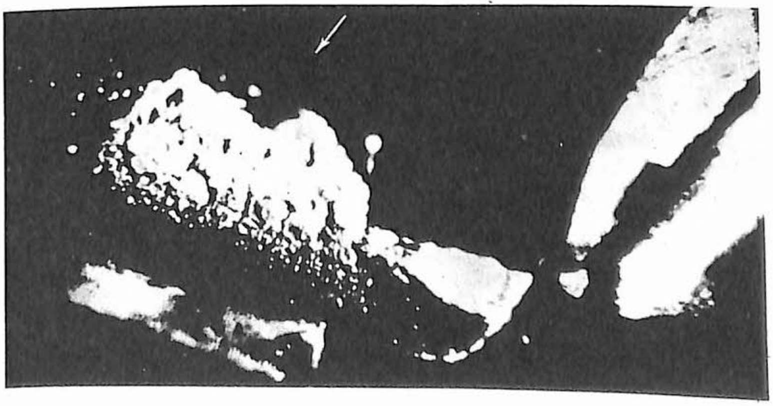
The synthesis of plutonium

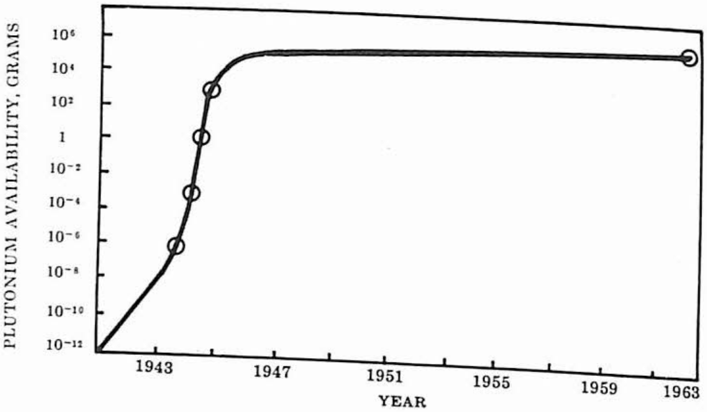
Plutonium-weighing balance. This quartz fiber balance was initially used for weighing plutonium. It has a sensitivity of 0.0003 mg.



Lawrence Radiation Laboratories

First plutonium compound to be weighed (September 10, 1942). This bit of plutonium oxide, magnified 85 times and indicated by the arrow, weighed 2.77 mg. It lies near the end of a platinum weighing boat which is held by a forceps





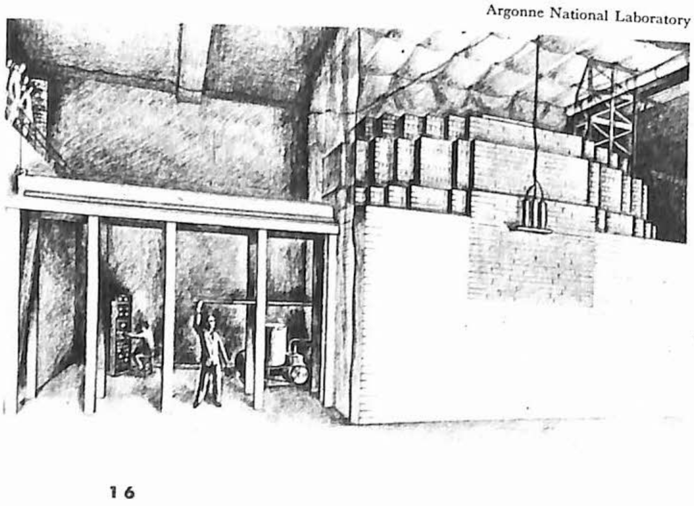
From picograms to tons—the growth in plutonium production

we were forced by the crowds of sight-seers wanting an early look at the new element to color some of the more plentiful aluminum hydroxide with green ink in order to devote our entire small supply of plutonium to the required, more urgent experiments. We preserved our integrity with the careful statement that "This *represents* a sample of plutonium hydroxide."

In one instance plutonium cooperated in a puzzling way. We were looking for a tetrapositive phosphate compound analogous to plutonium phosphate as a carrier. Instead bismuth phosphate with its tripositive bismuth, noncorrosive, and good handling properties, turned out to be an excellent carrier for tetrapositive plutonium. This was an unexpected windfall in our urgent efforts to develop completely reliable chemical separation processes for use at Hanford.

The world's first reactor. Because of wartime secrecy no photographs are available. The reactor itself was composed of layers of graphite and uranium, piled on one another, and thus the early name for reactors became "piles." Criticality (self-sustained chain reaction) was achieved when the 57th layer was added. News of the accomplishment was immediately telephoned to Washington in cryptic language: "The Italian navigator has landed in the new world and found the natives very friendly."

Argonne National Laboratory



Because of this puzzling behavior, there were many persistent doubts that the bismuth phosphate process could be made to work at the Hanford Plant levels of plutonium concentration. Therefore a crucial test of the process on the ultramicrochemical scale was done, using cyclotron-produced plutonium. Then, when larger amounts of plutonium were available a complete mechanical test of the Hanford process was carried out on the semiworks scale. Still some skeptics thought the process would never work at high concentrations, some backing their convictions with bets. Some held onto these convictions until the day that the first successful production run was completed.

The scale-up from the ultramicrochemical experiments to the final Hanford plant amounts to a factor of a billion billion, surely the greatest scale-up ever attempted. In spite of these difficulties the chemical separations process at Hanford was successful from the beginning, and its performance exceeded all expectations. High yields and decontamination factors were achieved in the very beginning and continued to improve with time.

We proceeded with the utmost respect for the formidable dangers involved in separating out the ornery element. The chemical plants were massive structures ingeniously engineered to fit the serious problems inherent in handling the extremely high levels of radioactivity. It is self-evident that no one saw the plutonium as it entered the plant. It is also true that no one saw it until just before it finally emerged as a relatively pure compound. In the meantime, it had passed through a maze of extraction vessels via thousands of feet of piping with only instruments and an occasional sampling to chart its progress. Probably no process on a grand scale in chemical engineering history received such painful care in its development and engineering designs as that exercised in the Hanford plutonium plant.

Despite the cussedness of plutonium, we were able to carry out this enormous effort without getting too far out of line, bureaucratically speaking. One exception had to do with our concern for finding a long-range alternate to the bismuth phosphate process, one that would recover the uranium for reuse. In developing the Redox process we conveniently ignored great official resistance from the Manhattan District and carried on a large-scale bootleg research effort during much of 1945. Both the bismuth phosphate and the Redox processes were used at Hanford.

The Present and Future

Certainly plutonium is no less cantankerous today than it was when we were battling and overcoming the many difficulties during World War II, but we have learned much more about the element's potentialities as a useful servant of man. Indeed I predict that plutonium—ornery and unusual as it is—will turn out to be one of the most useful elements at our command. The really important aspect of plutonium-239 is that it is a fissionable isotope which can be produced from uranium-238, an isotope that is not readily fissionable. It is evident that gas, oil and coal are not inexhaustible, but rather that the supplies of these fuels are eventually limited. The energy locked in uranium is at least a thousandfold more than that in our usable reserve of fossil fuels. This is calculated, however, assuming utilization not only of the 0.7% uranium-235 present, but also the inherent energy in the 99.3% of uranium-238. Thus the immense importance of a reactor capable of producing more fuel than it consumes, comes into sharp focus when we look at the future of a scientific and technological society inescapably dependent on the large-scale consumption of energy. Plutonium will play a principal role in the drama of our future technological growth.

Plutonium will also be called upon to play another role as exemplified by the PRTR (plutonium recycle test reactor) at Hanford. The recycling of plutonium produced in water reactors or in other, advanced converter, reactors can provide a significant improvement in fuel utilization.

But with its use in reactors, plutonium shows its ornery property. One of the greatest barriers to developing breeder reactor technology is plutonium's combination of high radioactivity, amounting to about 140,000,000 alpha disintegrations per minute per milligram, and its physiological property of depositing in the bones and remaining there. Even today, chemical investigations of plutonium are frequently carried out on a scale of a milligram or less by choice, rather than from any limitation of supply. These deadly properties of plutonium mean that very elaborate systems of remote control must be used in every phase of its handling. It is a special tribute to the workers at Hanford that in their unremitting carefulness no one has ever been hurt. I am sure that the difficulties which plutonium's radioactivity poses for its widespread use in nuclear power will similarly be overcome as a result of the ever-increasing sophistication of automation.

The development of plutonium reactor technology, of course, involves many other difficulties. The reactors must be run at a high temperature so that the energy can be usefully and efficiently extracted. Construction materials and corrosion present other problems.

Most of us have read of the phoenix, that mythical bird of the Egyptians which when consumed by fire arises again from its own ashes. Plutonium promises to provide us with a phoenix-like fuel. This fuel, being developed at Hanford and containing certain combinations of the plutonium isotopes 239, 240, and 241 is expected to make possible extraordinarily long-lived reactor cores. As plutonium-239 is burned in the reactor, the fertile plutonium-240 isotope yields enough fissionable plutonium-241 to maintain the reactivity of the fuel.

When an element shows the versatility of plutonium, we can afford to put up with considerable orneriness.

This article is based on an address delivered by Dr. Seaborg before the Meeting on the Commercial Fabrication of Plutonium Fuel in Richland, Wash.

GLENN T. SEABORG, Chairman of the U.S. Atomic Energy Commission, received a Ph.D. in chemistry from the University of California in 1937. From 1940 to 1958 he helped to discover the transuranium elements, plutonium, neptunium, americium, curium, berkelium, californium, einsteinium, fermium, and mendelevium. Also, Dr. Seaborg and his colleagues are responsible for identifying more than 100 isotopes of elements throughout the periodic table; with the information gathered in his laboratories, radioactivity characteristics have been predicted for many isotopes of elements which still have not been found. Under his leadership, entirely new methodologies and instrumentation have been developed which have become the cornerstone of nuclear chemistry. In 1951, with E. M. McMillan, Dr. Seaborg was awarded the Nobel prize in chemistry.

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CHEMISTRY OF THE NOBLE GASES*

By Professor N. N. GREENWOOD, M.SC., SC.D., F.R.I.C.
University of Newcastle upon Tyne

The inert gases, or noble gases as they are now more appropriately called, are a remarkable group of elements. The lightest, helium, was recognized in the gases of the sun before it was isolated on earth as its name (ἥλιος) implies. The first inert gas was isolated in 1895 by Ramsay and Rayleigh; it was named argon (ἀργός, inert) and occurs to the extent of 0·93% in the earth's atmosphere. The other gases were all isolated before the turn of the century and were named neon (νέου, new), krypton (κρυπτόυ, hidden), xenon ξένου, stranger) and radon (radioactive emanation). Though they occur much less abundantly than argon they cannot strictly be called rare gases; this can be illustrated by calculating the volumes occupied at s.t.p. by the gases in this lecture theatre (volume $\simeq 10^6$ litres): helium 5·24 l, neon 18·3 l, argon 9,340 l, krypton 1·14 l and xenon 87 ml.

A few characteristic properties are listed in Table I, which shows that the inert-gas atoms have complete *s* and *p* subshells. For this reason there are only weak van der Waals interactions between the individual atoms and this leads to the very low boiling points and heats of vaporization shown. The ionization potentials (energy required to remove one electron from an atom to give a cation, M^+) are very high compared with those of the alkali metals (90–124 kcal/mole). In fact, all attempts to prepare well-defined stoichiometric chemical compounds of these elements were unsuccessful, and for over 60 years they epitomized chemical inertness. Indeed, their electron configuration, s^2p^6, became known as 'the stable octet,' and this formed the basis of the first electronic theory of valency in 1916. Despite this, many people felt that it should be possible to induce the inert gases to form compounds, and many of the early experiments directed to this end have recently been reviewed.[1]

TABLE I

SOME PROPERTIES OF THE NOBLE GASES

At. No.		Electron config.	Ionization potential (kcal/mole)	Boiling point (°C)	ΔH_{vap} (kcal/mole)
He	2	$1s^2$	567	−269	0·022
Ne	10	$2s^22p^6$	497	−246	0·44
Ar	18	$3s^23p^6$	363	−186	1·50
Kr	36	$4s^24p^6$	323	−153	2·31
Xe	54	$5s^25p^6$	280	−107	3·27
Rn	86	$6s^26p^6$	247	−65	4·3

There were several reasons why chemists believed that the inert gases might form chemical compounds under the correct conditions. For example, the ionization potential of xenon is actually lower than those of hydrogen, nitrogen, oxygen, fluorine and chlorine, all of which readily form covalent compounds (Xe 280, H 313, N 335, O 314, F 402, Cl 300 kcal/mole). Furthermore, the ionization potential of radon is very similar to that of mercury, which readily forms cationic species (Rn 247, Hg 240 kcal/mole). There were also suggestive experimental observations. Thus, we are all familiar with the fact that iodine is virtually insoluble in water but dissolves freely in the presence of potassium iodide to give the brown I_3^- anion. The iodide ion I^- has exactly the same number of electrons as xenon, which might therefore be expected to behave very similarly; apparently it does not. The existence of stable interhalogen compounds, such as BrF_3, IF_5 and IF_7, also indicates that more electrons than are allowed by the classical octet theory can be involved in bonding and that the isoelectronic species, such as KrF_2, XeF_4 and XeF_6, might be capable of independent existence.

Finally, there was the possibility of forming co-ordination complexes by donating a pair of electrons from an inert-gas atom to another atom. After all, the inert gases are bristling with lone-pairs and their ionization potentials are often no greater than those of ammonia, water, ethylene and other well-known ligands. However, recent detailed studies of the interaction of xenon and krypton with powerful electron-pair acceptors, such as boron trifluoride and trichloride, indicated that there is no specific donor–acceptor bond-formation even at very low temperatures.

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* This article is based on a lecture given to sixth-form pupils on 20 and 25 November, 1963, and to the Bedson Club of the University of Newcastle upon Tyne on 6 December, 1963.

This was the position at the beginning of 1962. Then, in June of that year, N. Bartlett announced[2] that when xenon was placed in contact with gaseous platinum hexafluoride at room temperature an immediate reaction occurred to give an orange-yellow solid:

$$\mathrm{Xe\,(g) + PtF_6\,(g) = XePtF_6\,(s)}$$

Xenon hexafluoroplatinate(v) was the first authentic compound of a noble gas. The idea was taken up by dozens of different laboratories throughout the world, and within 18 months a 400-page book on the subject had been published.[3] This gives some idea of the speed at which modern advances in chemistry are made.

The first group to start work after the initial discovery was one at the Argonne National Laboratory in Chicago, and three months after Bartlett's paper they reported[4] that xenon combined directly with fluorine when the two gases were heated in a nickel vessel under pressure at 400°:

$$\mathrm{Xe\,(g) + 2F_2\,(g) = XeF_4\,(s)}$$

The compound can even be made simply by passing a mixture of xenon and fluorine diluted with nitrogen through a nickel tube heated with a bunsen burner; white crystals of xenon tetrafluoride sublime out—an experiment that could have been done at any time during the past 60 years!

TABLE II

PROPERTIES OF THE XENON FLUORIDES

Property	XeF_2	XeF_4	XeF_6
M.p. (°C)	140	114	46
Density (g/ml)	4·32	4·04	—
Sol. in liq. HF at 25° (g/100 g)	175	4	250
Heat of solution (kcal/mole)	2·5	6·7	18
Vap. press. (mm Hg at 25°) ..	3	4	30
Heat of sublimation (kcal/mole)	12·3	15·3	9·0
Bond length Xe–F (Å) ..	2·00	1·95	1·91

About 20 compounds of xenon have now been isolated and many more identified in reaction systems. Compounds of krypton and radon have also been made, and a systematic account of this new area of chemistry will now be given. Detailed references to the original literature are given in refs 1, 3, 5 and 6. It will be convenient to break up the discussion into three parts:

(1) Preparation, physical properties and structures;

(2) Chemical reactions;

(3) Stability and bonding theory.

PREPARATION, PHYSICAL PROPERTIES AND STRUCTURES

Xenon Difluoride

XeF_2 is a white crystalline compound which is most simply prepared by irradiating a mixture of xenon and excess fluorine for one day at 25° and 1½ atm pressure with light from a high-pressure mercury arc. It is important to freeze out the product at −78° as it forms, otherwise some xenon tetrafluoride is also formed, and these two compounds are very difficult to separate. Amounts up to 10 g can be prepared in this way in silica vessels or in nickel vessels with sapphire windows. The compound can also be prepared by irradiating a xenon–fluorine mixture with ^{60}Co γ-rays, or by circulating a 1 : 4 mixture of the gases through a heated nickel tube at 400° and trapping the product at −50°. Some properties of xenon difluoride are summarized in Table II. It can be seen that the melting point, 140°, is far above the m.p. of both xenon (−111°) and fluorine (−223°) and the density is also greater than that of solid xenon (3·1) or fluorine (1·3). Xenon difluoride has a very high solubility in anhydrous hydrogen fluoride, in which it is non-conducting.

The vapour pressure is sufficient to allow the compound to sublime readily when warmed under vacuum and it forms beautiful crystals in this way. The heat of vaporization (12·3 kcal/mole) suggests that there is appreciable separation of charge within the molecule, and this coulombic attraction contributes to the low volatility (cf. ΔH_{vap} Xe

3·27, F_2 1·64 kcal/mole). Xenon difluoride is diamagnetic, indicating that there are no unpaired electrons in the structure.

Neutron diffraction and X-ray diffraction have shown that xenon difluoride crystallizes in the tetragonal system with cell constants $a = 4·315$ and $c = 6·990 \pm 0·004$ Å, and two molecules in the unit cell, as illustrated in Fig. 1. The XeF_2 molecule is linear and this is also consistent with the infra-red and Raman vibrational spectra (both band shapes and occurrence). The modes of vibration are shown in Fig. 2.

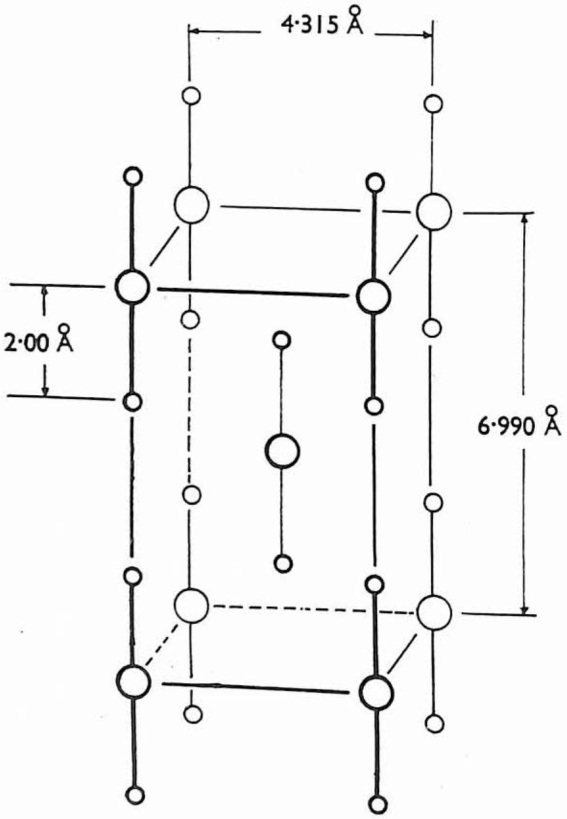


Fig. 1. Crystal structure of XeF_2

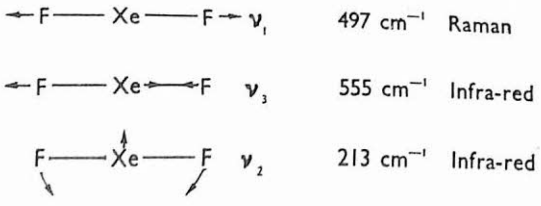


Fig. 2. Vibrational spectrum of XeF_2

Xenon Tetrafluoride

XeF_4 is best prepared by heating xenon and fluorine in an atom ratio of 1:5 at 13 atm and 400° in a nickel weighing-can for 1 hr. Up to 50 g can be handled and the yield is quantitative. Flow methods through a nickel tube, electrial discharge methods and γ-irradiation have also been used. The compound sublimes readily under reduced pressure and is obtained as beautifully-formed colourless crystals.

The properties of xenon tetrafluoride are summarized in Table II. Comparison with xenon difluoride shows that the tetrafluoride has a lower m.p. and density, and a considerably lower solubility in anhydrous hydrogen fluoride; the heat of vaporization, however, is 25 per cent higher. Neutron diffraction and X-ray diffraction results indicate that the tetrafluoride crystallizes in the monoclinic system with two molecules in the unit cell, as shown in Fig. 3. The molecule is square-planar with the F–Xe–F bond angle 90°, and the Xe–F bond distance slightly less than that for the difluoride. The molecules pack in a body-centred array, and the angle between the planes of the two sets of molecules is 55·2°.

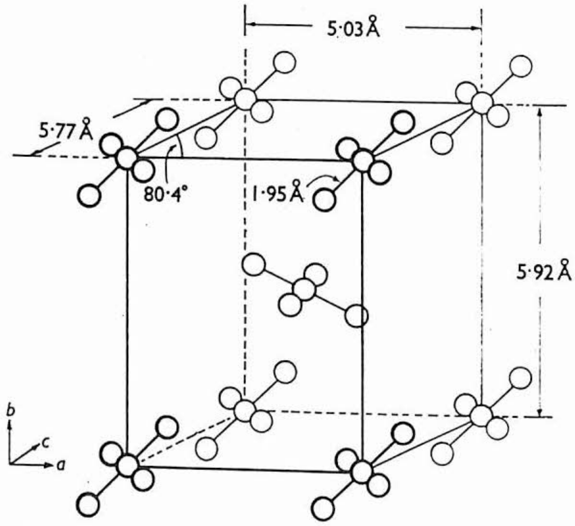
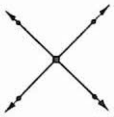
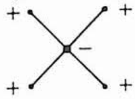
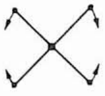
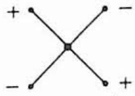
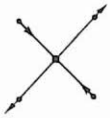
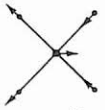
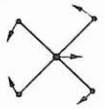


Fig. 3. Crystal structure of XeF_4 ('exploded' view)

The infra-red and Raman spectra of xenon tetrafluoride are also best interpreted on the basis of a square-planar model. Details are given in Table III. A molecule containing five atoms should have nine (*i.e.* $3n-6$) modes of vibration, but if it has square-planar symmetry two pairs of these should be doubly degenerate, that is, have the same energy; ν_6 represents one of these pairs and ν_7 the other, so that only seven fundamental modes are expected, of which one, ν_4, is inactive in both infra-red and Raman and can only be observed as an overtone. It will also be seen that no fundamental vibration in the infra-red appears in the Raman spectrum and vice versa. This 'rule of mutual exclusion' indicates that the molecule has a centre of symmetry and confirms that it is not tetrahedral. (A tetrahedral molecule gives rise to only four fundamental modes, all of which give Raman lines and two of which also give lines in the infra-red; the infra-red modes are triply degenerate and one of the Raman modes is doubly degenerate, making a total of nine modes in all, as required for a pentatomic molecule.)

TABLE III

VIBRATION SPECTRUM OF XENON TETRAFLUORIDE

ν_1 (R)	543 cm^{-1}	
ν_2 (I.R.)	291 cm^{-1}	
ν_3 (R)	235 cm^{-1}	
ν_4 inactive	(221 cm^{-1})	
ν_5 (R)	502 cm^{-1}	
ν_6 (I.R.)	586 cm^{-1}	
ν_7 (I.R.)	123 cm^{-1}	

(R) = Raman; (I.R.) = Infra-red

Xenon Hexafluoride

XeF_6 is less stable than the difluoride and tetrafluoride. It has been prepared in 10-g amounts by heating xenon in a large excess of fluorine at pressures up to 200 atm and temperatures of 300–400°. In a typical experiment a 95 per cent yield of xenon hexafluoride was obtained by heating $Xe + 20\ F_2$ for 16 hr at 300° and 60 atm. Electric-discharge methods have also been used. Some properties of xenon hexafluoride are listed in Table II. The low m.p. and high solubility in anhydrous hydrogen fluoride are noteworthy. Unlike solutions of the difluoride and tetrafluoride, these solutions are good conductors of electricity. The high vapour pressure and low heat of vaporization reflect the more symmetrical structure of this molecule. Xenon hexafluoride is thermochroic: the colourless crystals turn pale yellow at 42° and melt to a yellow liquid; the vapour is a pale yellow-green. All these changes are reversible and find explanation in terms of the detailed theory of bonding and the energy-level diagram for the compound.

X-ray and neutron-diffraction studies have proved difficult because of the reactivity of the hexafluoride. For example, glass, silicon and mercury are all rapidly attacked. However, the structure is certainly octahedral, though it is not yet certain whether all bond lengths are equal. The infra-red and Raman spectra have also only been partly elucidated; there appear to be no coincidences, indicating a centrosymmetrical molecule. The Xe–F symmetric stretching vibration occurs at 655 cm^{-1} in the Raman spectrum and the Xe–F antisymmetric stretching mode is at 612 cm^{-1} in the infra-red.

Other Xenon Fluorides

Irradiation of xenon tetrafluorides with ^{60}Co γ-rays at $-196°$ yields xenon monofluoride radicals, XeF, trapped in the crystal lattice. This species, which is stable only at low temperatures, has one unpaired electron; it is paramagnetic and colours the host lattice bright blue.

Crystals of composition XeF_3 can be grown from the vapour of xenon tetrafluoride containing some difluoride. The compound is diamagnetic (no unpaired electrons) and colourless. X-ray crystallography shows that the lattice consists of equal numbers of XeF_2 and XeF_4 units packed so that the xenon atoms form a face-centred array. The crystals are monoclinic with cell dimensions $a = 6{\cdot}64$ Å, $b = 7{\cdot}33$ Å, $c = 6{\cdot}40$ Å, $\beta = 92° 40'$. The density is 4·02 g/ml and all bond distances and bond angles are normal.

The preparation of xenon octafluoride has been claimed but not confirmed. Thus, when xenon was heated with 16 mole-equivalents of fluorine at 620° and 200 atm and the reaction vessel then chilled to −78°, yellow crystals of composition $XeF_{7{\cdot}9 \pm 0{\cdot}3}$ were said to be isolated. At room temperature the compound is apparently an unstable yellow gas.

Xenon Oxytetrafluoride

$XeOF_4$ is formed when xenon hexafluoride is kept in glass or silica vessels:

$$2XeF_6 + SiO_2 = 2XeOF_4 + SiF_4$$

Xenon hexafluoride reacts completely with quartz at 50° in two days. The stoichiometric amount of water vapour also hydrolyses the hexafluoride to this product:

$$XeF_6 + H_2O = XeOF_4 + 2HF$$

Xenon oxytetrafluoride is a clear, colourless liquid at room temperature. It freezes to a white solid at −40° (or −28°) and has a vapour pressure of 8 mm at 0° and 29 mm at 23°. The heat of vaporization is approximately 9 kcal/mole.

The infra-red and Raman spectra establish that the molecule is a square-based pyramid C_{4v} symmetry) as shown in Fig. 4. The detailed assignments are listed in Table IV, from which it can be seen that there are several coincidences in the Raman and infra-red spectra, consistent with the absence of a centre of symmetry. The spectra of the oxytetrafluoride should also be compared with those of xenon tetrafluoride in Table III; there is a marked similarity except for the two extra bands associated with the Xe–O stretching and wagging modes. Force-constant calculations clearly indicate the double-bond character of the Xe=O bond. Similarity with the isoelectronic interhalogen compound, bromine pentafluoride, is also noteworthy.

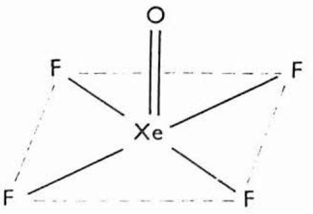


Fig. 4. Structure of $XeOF_4$

The molecular integrity of xenon oxytetrafluoride has been further demonstrated in a time-of-flight mass spectrometer which also indicated the presence of the species XeO_2F_2. In both these compounds xenon is in the oxidation state VI. Another oxyfluoride, $XeOF_2$, in which it is in the oxidation state IV, is formed when xenon reacts with oxygen difluoride in an electric discharge, but little is known of its properties.

$$Xe + F_2O = XeOF_2$$

Xenon Trioxide

XeO_3 was first prepared by an undergraduate at Berkeley University; it was

TABLE IV

VIBRATIONAL SPECTRUM OF XENON OXYTETRAFLUORIDE

Mode	Raman (liquid) cm⁻¹	I.R. (gas) cm⁻¹	Assignment
ν_1	919 (s, p)	928 (s)	Xe–O stretch
ν_2	566 (vs, p)	578 (w)	Xe–F_4 symmetric stretch
ν_3	286 (vw,p)	288 (s)	Xe–F_4 sym. out-of-plane deformation
ν_4	231 (w, dp)	inactive	Xe–F_4 sym. in-plane deformation
ν_5	530 (s, dp)	inactive	Xe–F_4 out-of-phase stretch
ν_6	not obs.	inactive	Xe–F_4 antisym. out-of-plane deformation
ν_7	not obs.	609 (vs)	Xe–F_4 antisym. stretch
ν_8	364 (mw, dp)	362 (ms)	Xe–O wag
ν_9	161 (vw, dp)	not obs.	Xe–F_4 antisym. in-plane deformation

vw, very weak; mw, medium-weak; w, weak; ms, medium-strong; s, strong; vs, very strong; p, polarized; dp, depolarized.

obtained as white, non-volatile, highly-explosive crystals by evaporating the aqueous acid hydrolysate of xenon tetrafluoride. During the hydrolysis about half of the Xe^{IV} disproportionates into Xe^{0} and Xe^{VI}, and the other half oxidizes water to oxygen; the overall reaction can be represented approximately by the equation:

$$3XeF_4 + 6H_2O = 2Xe + \tfrac{3}{2}O_2 + XeO_3 + 12HF$$

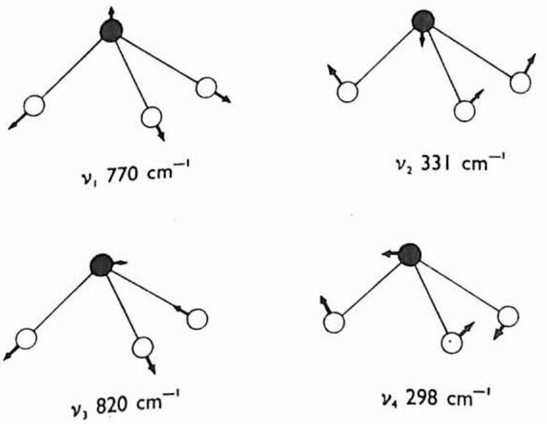
The trioxide can also be prepared by slow hydrolysis of the hexafluoride:

$$XeF_6 + 3H_2O = XeO_3 + 6HF$$

The degree of hydration of the trioxide is unknown but oxygen atoms can be exchanged by equilibration with ^{18}O-enriched water, and it seems probable that the reaction is

$$XeO_3 + 3H_2O \rightleftharpoons Xe(OH)_6$$

X-ray structural work on the crystals shows that xenon trioxide has an orthorhombic unit cell with $a = 6{\cdot}163 \pm 0{\cdot}008$ Å, $b = 8{\cdot}115 \pm 0{\cdot}010$ Å and $c = 5{\cdot}234 \pm 0{\cdot}008$ Å. There are four molecules in the unit cell and the density is 4·55 g/ml. XeO_3 is a trigonal pyramidal molecule as shown in Fig. 5. The bond length Xe–O is 1·76 ± 0·04 Å and the bond angle O–Xe–O is approximately 103°. The molecular symmetry and dimensions are very similar to those of the isoelectronic iodate ion, IO_3^-, for which the mean bond lengths and bond angles are 1·82 Å and 97°.



ν_1 770 cm^{-1} ν_2 331 cm^{-1}

ν_3 820 cm^{-1} ν_4 298 cm^{-1}

Fig. 5. Vibrational spectrum of XeO_3

Infra-red assignments are shown in Fig. 5. There is a marked similarity to the spectra of the ions ClO_3^-, BrO_3^- and IO_3^-, and the principal stretching-force constant indicates considerable double-bond character, consistent with the short Xe–O bond distance.

Xenon Tetroxide

XeO_4 is a volatile yellow solid, unstable at room temperature. It is prepared[7] by adding sodium or barium perxenate (*see* next section) to anhydrous sulphuric acid at −5°, the reaction being formally represented by the equation:

$$Ba_2XeO_6 + 2H_2SO_4 = XeO_4 + 2BaSO_4 + 2H_2O$$

Yields of up to 34 per cent (0·1 g) were obtained.

The xenon tetroxide molecule is tetrahedral (like osmium tetroxide and the periodate ion, IO_4^-) and has two infra-red active vibrations as expected: ν_3, 877 cm^{-1}; ν_4, 305·7 cm^{-1}. The vapour pressure is 3 mm at −35° and 25 mm at 0°, which corresponds to a heat of sublimation of 8·0 kcal/mole.

Compounds of Krypton and Radon

Compounds of krypton are less stable than those of xenon and this has limited the amount of attention they have received. Compounds of radon may well prove to be more stable, but difficulties of handling this highly radioactive element have also precluded extensive investigation.

Krypton, unlike xenon, does not react with platinum hexafluoride at temperatures up to 50° nor does it react when heated with fluorine. However, the species KrF_2 has been identified by matrix-isolation techniques. A mixture of fluorine and krypton with argon as the matrix was sprayed on to a caesium-iodide window at −253° and then irradiated with ultra-violet light. Bands appearing in the infra-red spectrum could be assigned to the linear molecule KrF_2: ν_3, 580 cm^{-1}; ν_2, 236 cm^{-1}.

Krypton tetrafluoride, KrF_4, is said to be formed as transparent, colourless crystals when an electric discharge is passed through a gaseous mixture of the elements. Thus, when a mixture of composition Kr + $2F_2$ at 12 mm pressure was passed through an arc of approximately 1,000 V/30mA between copper electrodes and the products trapped out at −188°, a yield of 1·15 g KrF_4 was obtained in 4 hr. The compound has a vapour pressure of 4 mm at −30°, 30 mm at 0° and 90 mm at 20°, and a heat of sublimation of 8·8 kcal/mole. At 20° one-tenth of a sample of krypton tetrafluoride decomposed in one hour and decomposition was very rapid above 60°.

Hydrolysis of krypton tetrafluoride at room temperature results in the liberation of krypton and oxygen:

$$KrF_4 + 2H_2O = Kr + O_2 + 4HF$$

However, slow hydrolysis by ice at −30° to −60° gave 2–3 per cent of an acid whose stable barium salt could be isolated at room temperature.[8] Hydrolysis of krypton tetrafluoride with aqueous barium hydroxide at 0° gave a 7 per cent yield of a compound considered to be barium kryptate, $BaKrO_4$. The acid may be KrO_3,xH_2O, for example $Kr(OH)_6$; as the stoichiometric formula of the acid and the oxidation state of the krypton have not yet been established it is perhaps appropriate to call it kryptic acid.

Tracer experiments at the 10–100 μc level indicate that a radon fluoride, RnF_x, can be prepared from mixtures of the gases at 400° but the stoichiometry of the reaction has not yet been established. Radon fluoride is stable, distils at 230–250°/10^{-6} mm and appears to be an ionic compound. It is reduced by hydrogen to radon and hydrogen fluoride at 500°. Attempts to prepare radon chloride and radon oxide by thermal or photochemical means have so far been unsuccessful.

CHEMICAL REACTIONS OF XENON COMPOUNDS

The chemical reactions of the compounds of xenon have been extensively studied and some typical examples will now be discussed.

Non-aqueous Chemistry

The fluorides of xenon react quantitatively with hydrogen at about 400° and this has been used as a method of analysis.

$$\begin{aligned} XeF_2 + H_2 &= Xe + 2HF \\ XeF_4 + 2H_2 &= Xe + 4HF \\ XeF_6 + 3H_2 &= Xe + 6HF \end{aligned}$$

Xenon oxytetrafluoride reacts similarly with a large excess of hydrogen at 350°:

$$XeOF_4 + 3H_2 = Xe + H_2O + 4HF$$

Reaction with gaseous hydrogen chloride is much more rapid and can be carried out even at −78°:

$$XeF_4 + 4HCl = Xe + 4HF + 2Cl_2$$

It is noteworthy that no indication of a xenon chloride was detected in this reaction.

Xenon tetrafluoride is a good fluorinating agent; it attacks mercury at room temperature and a solution of the tetrafluoride in anhydrous hydrogen fluoride reacts quantitatively with platinum:

$$\begin{aligned} XeF_4 + 2Hg &= Xe + 2HgF_2 \\ XeF_4 + Pt &= Xe + PtF_4 \end{aligned}$$

Likewise the tetrafluoride fluorinates boron trichloride to a mixture of boron chloride fluorides, BCl_xF_{3-x}, and carbon tetrachloride yields CCl_3F. Nitrogen dioxide is fluorinated to nitryl fluoride, whereas sulphur tetrafluoride and selenium tetrafluoride are slowly oxidized to the corresponding hexafluorides:

$$\begin{aligned} XeF_4 + 4NO_2 &= Xe + 4NO_2F \\ XeF_4 + 2SF_4 &= Xe + 2SF_6 \\ XeF_4 + 2SeF_4 &= Xe + 2SeF_6 \end{aligned}$$

Liquid ammonia ignites and reacts explosively on contact with xenon tetrafluoride; xenon, nitrogen and ammonium fluoride are among the products. The reaction can be represented formally as the initial formation of hydrogen fluoride, which then reacts with excess of ammonia to form ammonium fluoride:

$$\begin{aligned} 3XeF_4 + 4NH_3 &= 3Xe + 12HF + 2N_2 \\ 12HF + 12NH_3 &= 12NH_4F \end{aligned}$$

Xenon tetrafluoride is itself quantitatively oxidized by dioxygen difluoride at −78° according to the equation:

$$XeF_4 + O_2F_2 = XeF_6 + O_2$$

This reaction represents a 'chemical' synthesis of a xenon fluoride which involves fluorination with a compound of fluorine rather than by the element itself. Other chemical syntheses have also been achieved. Thus, when xenon is heated with 2·2 mole-equivalents of CF_3OF at 250 atm and 225°.

xenon difluoride is formed. A similar reaction with FSO_2OF at 150 atm and 175° also produces xenon difluoride. The same compound is formed when xenon and carbon tetrafluoride are passed through an electric discharge.

It will be recalled that the first authentic example of a stoichiometric compound of a noble gas was xenon hexafluoroplatinate, $XePtF_6$. Similar compounds are formed by other reactive hexafluorides, *e.g.* $XeRhF_6$ (deep red), $XeRuF_6$ and $XePuF_6$. However, no compounds were formed with the stabler hexafluorides, IrF_6, UF_6 and NpF_6.

When xenon reacts with an excess of platinum hexafluoride other compounds are formed with compositions ranging up to $Xe(PtF_6)_2$, but their structure has not been definitely established and they have been formulated both as ionic and as fluorine-bridged covalent compounds: $Xe^{2+}(PtF_6^-)_2$ and $F_5Pt{-}F{-}Xe{-}F{-}PtF_5$. The ionic structure is suggested by the infra-red spectrum, which shows only two absorptions as expected for the PtF_6^- ion. This is also consistent with the fact that xenon hexafluoroplatinate(VI) reacts with rubidium fluoride in iodine pentafluoride as solvent to form the well-known orange-red salt, $RbPtF_6$. Likewise, caesium fluoride reacts with $Xe(PtF_6)_2$ in the same solvent to give $CsPtF_6$.

Pyrolysis (1 hr at 165°) of a solid having the composition $Xe(PtF_6)_{1 \cdot 8}$ gave xenon tetrafluoride and a new, brick-red, diamagnetic compound, $XePt_2F_{10}$.

Xenon tetrafluoride does not form complexes with sodium fluoride or potassium fluoride at temperatures up to 200° or with boron trifluoride at temperatures up to 100°. It therefore shows little tendency to act either as an electron-pair acceptor or an electron-pair donor (ligand). However, xenon tetrafluoride dissolves in antimony pentafluoride to give a gas and a yellow, diamagnetic complex, $XeF_2,2SbF_5$, m.p. 63°. The compound can be obtained directly from xenon difluoride and distils unchanged under reduced pressure at 120°. A similar straw-coloured complex, $XeF_2,2TaF_5$, m.p. 81°, is obtained from xenon tetrafluoride and tantalum pentafluoride. On the basis of their volatility and diamagnetism it seems probable that these adducts are bonded by bridging fluorine atoms, $F_5M{-}F{-}Xe{-}F{-}MF_5$.

Aqueous Solution Chemistry

The aqueous solution chemistry of xenon is fairly extensive and somewhat complicated. Species containing Xe^{VI} and Xe^{VIII} are well established and several salts have been isolated.

Xenon difluoride hydrolyses very slowly in water but more rapidly in alkaline solution:

$$XeF_2 + H_2O = Xe + \tfrac{1}{2}O_2 + 2HF$$

All the combined xenon is liberated as the element, indicating that 'hydrolysis' involves oxidation of water to oxygen and reduction of Xe^{II} to Xe^{0}.

Hydrolysis of the tetrafluoride gives varying products, depending on the conditons; hydrolysis is again accompanied by oxidation of water to oxygen and also by the disproportionation of xenon(IV) to higher and lower oxidation states. During the hydrolysis the surface of the tetrafluoride becomes bright canary-yellow, and this yellow solid dissolves with evolution of gas to give a colourless solution. The lifetime of the yellow solid is about 10 sec in alkaline solution, 8 min in water and 20 min in 3M sulphuric acid. About half of the tetrafluoride is used in oxidizing the water and about half disproportionates. The overall reaction can therefore be represented by the equation:

$$\begin{aligned}3XeF_4 &+ (6 + x)H_2O \\ &= 2Xe + \tfrac{3}{2}O_2 + XeO_3.xH_2O + 12HF\end{aligned}$$

Evaporation of the products of acid hydrolysis results in the isolation of xenon trioxide as noted in the previous section (p. 181). In the presence of barium carbonate, barium xenate (Ba_3XeO_6) is formed but this rapidly goes over to the perxenate, Ba_2XeO_6.

In contrast to the variable products isolated from simple hydrolysis experiments, the reaction with aqueous potassium iodide can be made quantitative under appropriate conditions, and this reaction has been used for analysis of the tetrafluoride:

$$XeF_4 + 4KI_{aq} = Xe + 2I_2 + 4KF$$

The liberated xenon was measured gas-volumetrically, the iodine determined by the usual thiosulphate titration, and the fluoride determined gravimetrically as calcium fluoride.

Hydrolysis of xenon hexafluoride with small amounts of water yields the oxytetrafluoride (*see* previous section, p. 180). Normally, however, the hexafluoride oxidizes water to oxygen and also disproportionates to Xe^{VIII} and lower oxidation states of xenon. Xe^{VIII} is fairly stable in alkaline solution but is unstable in acid, so that normally Xe^{VI} is the highest oxidation state in products of acid hydrolysis.

Perxenates can be prepared by titration of an aqueous solution of xenon trioxide with sodium hydroxide (0·5–18M); disproportionation occurs as indicated by the following overall equation:

$$2XeO_3 + 4NaOH + 6H_2O = Xe + O_2 + Na_4XeO_6,8H_2O$$

Potassium hydroxide gives the yellow, explosive complex, $K_4XeO_6,2XeO_3$.

Perxenates are more conveniently prepared by alkaline hydrolysis of xenon hexafluoride. The white sodium and barium salts are the most stable and from these the less-stable yellow salts of Pb^{2+} and UO_2^{2+} have been prepared metathetically. The least stable perxenate yet studied is the black silver salt which decomposes violently at 150°.

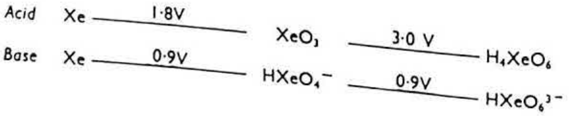
In common with the oxyacid salts of many other heavy elements, various perxenates can be obtained, the general formula being $M_{2n}XeO_{4+n},yH_2O$. Thus, salts of formulae $Na_4XeO_6,2H_2O$, $Na_4XeO_6,8H_2O$, Na_5HXeO_7 (*i.e.* $n = 2\frac{1}{2}$, $y = \frac{1}{2}$) and Na_6XeO_7,H_2O have been isolated. The integrity of several of these salts has been established by X-ray powder photography:

Formula	*Structure*	*a*	*b*	*c*
$Na_4XeO_6,2H_2O$	ortho-rhombic	6·25	5·77	10·28
$Na_4XeO_6,8H_2O$	ortho-rhombic	10·36	10·45	11·87
Na_5HXeO_7	cubic		$a_0 = 9{\cdot}391$	

The infra-red spectra of solid perxenates indicate that the ν_3 (antisymmetric stretching) mode of the XeO_6 group absorbs at 650–680 cm⁻¹. This is close to the value of the same mode in antimonates, tellurates and paraperiodates and indicates that the Xe–O bond in the XeO_6 complex is similar to the Sb–O, Te–O and I–O bonds in the octahedral groupings SbO_6, TeO_6 and IO_6.

The solubility of the dry sodium salt, Na_4XeO_6, in water at 25° is 7 g/l and in 0·5M sodium hydroxide 0·2 g/l. It is, however, perhaps a little early to anticipate the general use of perxenate as a gravimetric reagent for sodium!

As already indicated, solutions containing Xe^{VI} are strongly oxidizing. Iodide, bromide and chloride are all rapidly oxidized to the element, and iodine and bromine are then slowly oxidized to iodate and bromate. Manganese(II) is slowly converted to manganate and then permanganate. Fe^{II} is rapidly oxidized to Fe^{III} and Hg^{I} and Hg^{II} to Hg^{II}. As expected, perxenates, containing Xe^{VIII}, are even stronger oxidants. They oxidize more rapidly and take iodate to periodate; water is oxidized slowly in alkaline solution but rapidly in acid solution. These and similar observations enable the following approximate redox tables to be constructed:



STABILITY AND NATURE OF BONDING

Thermochemistry

The difluoride, tetrafluoride and hexafluoride of xenon are thermodynamically stable and are formed exothermically from their elements. The bonds in these compounds are chemical bonds with an energy content well within the normal range. It is known that the mean bond-energy E(Te–F) in TeF_6 is 78 kcal/mole and E(I–F) in IF_5 is 63 kcal/mole; extrapolation to the isoelectronic molecule XeF_4 might therefore lead one to expect E(Xe–F) in the range 20–40 kcal/mole, and this is observed.

The standard heat of formation of crystalline xenon tetrafluoride from gaseous xenon and fluorine has been determined by studying the reaction of xenon tetrafluoride with aqueous potassium iodide in a rocking bomb-calorimeter and analysing the contents after the reaction. The mean of four determinations gave:

$$-\Delta H_f^\circ(\text{XeF}_4\text{ cryst}) = 60{\cdot}1\text{ kcal/mole}$$

As the heat of sublimation of the tetrafluoride is 15·3 kcal/mole and the heat of dissociation of fluorine is 36·7 kcal/mole, then

$$-\Delta H_f^\circ(\text{XeF}_4\text{ gas}) = 44{\cdot}8\text{ kcal/mole}$$

and $E(\text{Xe–F})$ in $\text{XeF}_4 = 29{\cdot}6$ kcal/mole

The relevant thermochemical cycle is set out below (heat evolved is positive, heat absorbed is negative).

$$\begin{tikzcd}
\text{Xe(g)} + 2\text{F}_2\text{(g)} \arrow[d, "0\text{ kcal}"', "-73{\cdot}4\text{ kcal}"] \arrow[r, "+\,60{\cdot}1\text{ kcal}"] & \text{XeF}_4\text{(c)} \arrow[d, "-15{\cdot}3\text{ kcal}"] \\
\text{Xe(g)} + 4\text{F(g)} \arrow[r, "+\,118{\cdot}2\text{ kcal}"'] & \text{XeF}_4\text{(g)}
\end{tikzcd}$$

A second method, involving the reduction of xenon tetrafluoride with hydrogen at 130° in an isothermal calorimeter, gave a preliminary value for the heat of reduction of 202 kcal. This corresponds to $-\Delta H_f^\circ(\text{XeF}_4\text{ gas}) = 54{\cdot}8$ kcal/mole and a mean bond-energy $E(\text{Xe–F}) = 32{\cdot}0$ kcal/mole. This is in reasonable agreement with the independent value derived above.

The specific heat and heat capacity of xenon tetrafluoride have been measured between −263° and +27° and no anomalies were detected. At 25° the specific heat is 0·1367 cal/g, and the heat capacity, $C_p = 28{\cdot}334$ cal/mole. The measurements lead to the standard entropy, $S_{298}(\text{XeF}_4\text{ cryst}) = 35{\cdot}0 \pm 1$ cal deg^{-1} mole^{-1}, and hence to an entropy of formation, $\Delta S^\circ = 102{\cdot}5$ cal deg^{-1} mole^{-1}. The free energy of formation can then be obtained from the relation $-\Delta G_{298}^\circ = -\Delta H + T\Delta S = 29{\cdot}4$ kcal/mole, indicating the considerable thermodynamic stability of the tetrafluoride.

Reduction of xenon hexafluoride by hydrogen under similar conditions to those used for the tetrafluoride leads to the following results:

$$-\Delta H(\text{reduction}) = 306{\cdot}5\text{ kcal/mole}$$
$$-\Delta H_f(\text{XeF}_6\text{ gas}) = 78{\cdot}7\text{ kcal/mole}$$
$$E(\text{Xe–F})\text{ in XeF}_6 = 31{\cdot}5\text{ kcal/mole}$$

The fact that xenon hexafluoride is a 'normal,' unexceptional compound is further emphasized by comparing its mean bond energy with that of its neighbours in the Periodic Table.^{5} Thus, if the mean bond energies in SbF_3 (92 kcal), TeF_4 (86 kcal) and IF_5 (63 kcal) are plotted against atomic number and extrapolated by one unit to XeF_6, the 'predicted' bond energy is 31 kcal, close to the value observed.

The thermodynamic data for gaseous xenon difluoride at 1 atm and 250° have been calculated from the vibrational spectroscopic data given in Fig. 2. The free energy ($-\Delta G$) and entropy ($-\Delta S$) of formation are:

$$-\Delta G_{523}(\text{XeF}_2\text{ gas at 1 atm}) = 5{\cdot}510\text{ kcal/mole}$$
$$-\Delta S_{523}(\text{XeF}_2\text{ gas at 1 atm}) = 26{\cdot}96\text{ cal deg}^{-1}\text{ mole}^{-1}$$

From the relation $-\Delta G = -\Delta H + T\Delta S$, the heat of formation at 250° is

$$-\Delta H_{523}(\text{XeF}_2\text{ gas at 1 atm}) = 19{\cdot}6\text{ kcal/mole}$$

The value at 25° will be similar, and from this and the heat of dissociation of fluorine one obtains

$$E(\text{Xe–F})\text{ in XeF}_2 = 28{\cdot}2\text{ kcal/mole}$$

The similarity of the Xe–F bond energy in XeF_2 (28·2 kcal), XeF_4 (29·6–32 kcal) and XeF_6 (31·5 kcal) is noteworthy, as also is the apparent slight increase in bond energy with co-ordination number. This latter trend may well be within the experimental error of these diverse determinations (probably about ±2 kcal) but if substantiated is unusual, since increase in co-ordination number of an element almost invariably diminishes the mean bond energy.

Oxy-compounds of xenon are less stable with respect to formation from the elements than are the fluorides but this reflects the greater stability of the doubly-bonded oxygen molecule compared with fluorine rather than the weakness of the Xe–O bond. (The bond dissociation energy of oxygen is 118·5 and of fluorine 36·7 kcal/mole.)

From the heat of explosion of xenon trioxide as measured in a bomb calorimeter, the heat of formation was found to be:

$$-\Delta H_f^\circ(\text{XeO}_3\text{ cryst}) = -96 \pm 2\text{ kcal/mole}$$

Exact calculation of the mean bond energy $E(\text{Xe–O})$ would require a knowledge of the heat of sublimation, as shown by the following thermochemical cycle:

$$\begin{tikzcd}
Xe(g) \arrow[d, "0\text{ kcal}"'] & + & \frac{3}{2}O_2(g) \arrow[r, "-96\text{ kcal}"] \arrow[d, "-177\cdot8\text{ kcal}"] & XeO_3(c) \arrow[d, "\Delta H_{subl}"] \\
Xe(g) & + & 3O(g) \arrow[r, "(81\cdot8-\Delta H_{subl})"'] & XeO_3(g)
\end{tikzcd}$$

Hence E(Xe–O) in XeO_3 = 27·3 − $\frac{1}{3}\Delta H_{subl}$

The heat of sublimation is not measurable but if a plausible value of about 22 kcal is taken for this quantity then

E(Xe–O) in $XeO_3 \simeq 20$ kcal

This is somewhat smaller than the Xe–F bond energy but would not, by itself, confer explosive instability: the large endothermic heat of formation is due to the fact that the Xe–O bond energy is very much less than the O–O bond energy in molecular oxygen.

Extrapolations similar to those already mentioned suggest that the heats of formation of xenon chlorides, like that of xenon trioxide, would be negative. Likewise the heat of formation of krypton tetrafluoride from its elements should be approximately zero, but the difluoride is probably slightly exothermic.

Theories of Bonding

A satisfactory theory of bonding must explain convincingly not only the stoichiometry and shape of the noble-gas compounds but also deal adequately with the observed physical properties and bond energies. As the theory becomes more precise, confident predictions of the stable groupings of atoms should be forthcoming.

It is clear that van der Waals interactions are far too weak to explain the bonding in noble-gas compounds. Such interactions are normally only 1–5 kcal/mole whereas the observed bond energies are 20–30 kcal/mole. Nor does the assumption of ionic bonding adequately explain the energies involved. Even for xenon difluoride a simple calculation shows that the second-stage ionization potential is too large to confer stability on the structure $Xe^{2+}(F^-)_2$ and the similarity in mean bond energies and bond distances for XeF_2, XeF_4 and XeF_6 rules out the possibility of structures such as $Xe^{4+}(F^-)_4$ and $Xe^{6+}(F^-)_6$. Other lines of evidence against ionic bonding in these compounds are the observed crystal structures of XeF_2 and XeF_4, the volatility of the compounds and the absolute values of the bond distances, which are at least 0·3 Å shorter than would be predicted on the basis of the packing of ions.

The bonding in xenon difluoride can formally be considered in terms of the promotion of a $5p$ electron on xenon to a $5d$ level. However, the energies involved suggest that this is unlikely to occur to any appreciable extent, and calculations indicate that the $5d$ orbitals are rather too diffuse for good bonding anyway. It follows that further promotion to account for the tetra- and hexafluoride is even less favourable energetically. The valence-bond method then suggests the mixing in of other structures with these hybrids to improve the bond energy, *e.g.* $F{-}Xe^+F^-$ and $F^-Xe^+{-}F$, but this is not particularly satisfactory and in any event merely describes the ground state of the molecule and says nothing about its electronically excited states and hence its ultraviolet spectrum.[9] It should be noted, however, that this theory correctly predicts a linear molecule for the difluoride and a square-planar molecule for the tetrafluoride. It predicts a tetragonally distorted octahedron for the hexafluoride, and careful measurements are at present being undertaken to determine whether the structure of this compound is in fact a regular or an elongated octahedron.

The most satisfactory treatment of the bonding in xenon compounds is the molecular-orbital method. In this theory molecular orbitals are constructed from atomic orbitals on the xenon and fluorine atoms. The three criteria which determine whether a given set of atomic orbitals can combine to give molecular orbitals are:

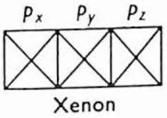
(*a*) the atomic orbitals should have similar energies;

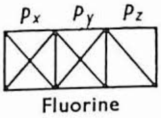
(*b*) they should have appreciable spatial overlap;

(*c*) they should have appropriate symmetry.

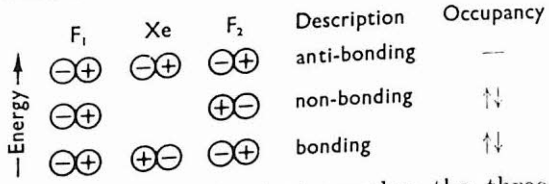
Molecular orbitals which have energies below the mean energy of the atomic orbitals from which they are constructed are called bonding molecular orbitals. Molecular orbitals which have energies close to those of the constituent atomic orbitals are called non-bonding molecular orbitals and those having energies above those of the constituent atomic orbitals are called anti-bonding molecular orbitals.

The theory can be illustrated by reference to xenon difluoride. The outer electronic configurations of xenon and fluorine are:





Let the molecular axis be the z axis. Then three atomic orbitals must be considered: the $5p_z$ orbital on the xenon atom and the $2p_z$ orbital on each of the fluorine atoms. These three atomic orbitals can combine to give three molecular orbitals, one of which is bonding, one non-bonding and one anti-bonding. The three atomic orbitals originally contained four electrons in all, *i.e.* two in the xenon $5p_z$ and one each in the two fluorine $2p_z$ orbitals. These four electrons are now placed so that two occupy the bonding molecular orbital and two occupy the non-bonding molecular orbital. The situation is illustrated in the following diagram:



It is clear that for best overlap the three atoms should lie in a straight line, as observed. Notice that the non-bonding orbital has no contribution from the xenon $2p_z$ orbital, since this has the wrong symmetry for combination, as indicated by the + and − signs. The approximate wave-mechanical description of these orbitals is:

$$\Psi_{ab} = \tfrac{1}{2}\psi(\mathrm{F}_1) + \frac{1}{\sqrt{2}}\psi(\mathrm{Xe}) + \tfrac{1}{2}\psi(\mathrm{F}_2)$$

$$\Psi_{nb} = \frac{1}{\sqrt{2}}\psi(\mathrm{F}_1) + 0\psi(\mathrm{Xe}) - \frac{1}{\sqrt{2}}\psi(\mathrm{F}_2)$$

$$\Psi_{b} = \tfrac{1}{2}\psi(\mathrm{F}_1) - \frac{1}{\sqrt{2}}\psi(\mathrm{Xe}) + \tfrac{1}{2}\psi(\mathrm{F}_2)$$

In these equations, b, nb and ab refer to bonding, non-bonding and antibonding molecular orbitals, Ψ, and the atomic orbitals, ψ, are labelled with an obvious notation. By squaring and adding the coefficients in each vertical and horizontal column it is simple to check that each atomic orbital has been used in all just once and that each molecular orbital is normalized to unity.

If the squares of the coefficients are taken to indicate the extent of electron occupancy, and if it is remembered that Ψ_b and Ψ_{nb} each contain two electrons, then it becomes apparent that the xenon atom has $2\left(\frac{1}{\sqrt{2}}\right)^2 = 1$ p_z-electron in its neighbourhood whereas the free atom had two; hence it has a resultant net change of $+1$. Likewise, each fluorine atom is associated with $\left[2(\tfrac{1}{2})^2 + 2\left(\frac{1}{\sqrt{2}}\right)^2\right] = 1\tfrac{1}{2}$ p_z-electrons, so that it has a resultant charge of $-1/2$. The theory thus enables us to calculate approximately the charge distribution within the molecule. A more precise calculation leads to a charge of $+1{\cdot}4$ on the xenon and $-0{\cdot}7$ on each fluorine. As a result of this partial separation of charges within the molecule, the heat of sublimation of xenon difluoride contains a substantial coulombic component in addition to the ubiquitous van der Waals attraction, and is therefore considerably greater than the heat of sublimation of xenon itself, as indicated in Tables I and II. Indeed, an estimate of the heat of sublimation based on an array of atoms in the positions indicated in Fig. 1 and carrying the partial charges calculated above gives excellent agreement with the experimental value.

An important consequence of the molecular-orbital bond theory is that it predicts enhanced stability the lower the ionization potential of the central atom and the more electronegative the outer atoms. Compounds of xenon and radon with fluorine and oxygen are therefore expected to be the most stable, whereas krypton fluorides or radon chloride should have only marginal stability. Compounds of argon and neon are not expected.

The molecular-orbital theory outlined above is in no way unique to inert-gas compounds or unusual in any of its features. It had previously been used to discuss bonding in the polyhalide ions, such as I_3^-, ICl_2^-, ICl_4^-, etc., and in many other situations. It can be extended to deal with compounds such as xenon tetrafluoride and xenon hexafluoride simply by forming three-centre molecular orbitals in the x and y directions as well as in the z direction. The theory therefore predicts a square-planar shape for XeF_4 and a regular octahedral shape for XeF_6. The similarities in bond lengths and bond energies for these compounds can also be understood. Partial charges on xenon and fluorine are approximately $+2$ and $-\frac{1}{2}$ in XeF_4; and $+2$ and $-\frac{1}{3}$ in XeF_6.

A final feature of the theory should be mentioned—its ability to help interpret ultra-violet and visible absorption spectra. Thus when an electron is excited from Ψ_{nb} to Ψ_{ab} it will absorb energy at a frequency defined by $\nu = \Delta E/\boldsymbol{h}$ where $\boldsymbol{h}$ is Planck's constant and ΔE is the difference in energy between the two levels. More extensive calculations also consider the molecular orbitals of π-symmetry,[9] and a detailed analysis of the various energy levels is at present being carried out for the complicated case of xenon hexafluoride which, as mentioned earlier, is thermochroic.

CONCLUSION

Speculations on potential applications of noble-gas compounds have been numerous. Are these compounds a means of storing fluorine in a readily available form; can they be used as oxidants in rocket-propellant systems or as specific fluorinating reagents in chemical reactions? The use of perxenates as powerful aqueous oxidants has already been mentioned. Specialized uses for shock-sensitive oxides such as xenon trioxide might be found. One of the most objectionable atomic-fission products is the volatile xenon isotope, ^{133}Xe; conversion to an involatile compound could make this available in megacurie amounts. Involatile radon needles for tumour therapy is another possibility.

Whatever the future applications of these compounds one thing is certain: the discovery that xenon readily forms a wide range of stable compounds has proved to be one of the most stimulating and significant observations in chemistry for many years. It has forced us to thin more deeply about the fundamentals of chemical bonding and has demonstrated in the most direct way possible how inadequate any 'stable octet' theory of valency must be. The stable octet, which was the first electronic theory of valency, was a great advance when it was originally expounded 50 years ago. It is disturbing to reflect that much elementary teaching of bond theory still relies on this concept despite the large areas of chemistry where it does not apply (*e.g.* ferrous and ferric compounds) and the many advances which have been made in our thinking during the last 40 years. An important lesson can also be learned from the fact that if, in 1962, a student had been asked 'What would happen if xenon were heated in the presence of fluorine?' and he had answered 'a volatile white crystalline solid of composition XeF_4 is formed quantitatively,' he would have been awarded no marks.

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Bonding in Xenon Hexafluoride

The recent discovery of xenon hexafluoride (*1–4*) has added another member to the family of intriguing xenon-fluorine compounds. There have been two main schools of thought concerning the theory of the bonding in the lower members: XeF_2 and XeF_4. The really distinguishing difference is that one group favored xenon $5d$ orbital hybridization[1] with its $5s$ and $5p$ orbitals (*5–8*); the other favored bonds involving primarily only the xenon $5p$ orbitals (*9–12*). That some investigators chose to express the formulation in terms of a separated electron pair or valence bond theory and others chose a molecular orbital description should *not* have materially affected the conclusions because it has long been established that complete valence bond calculations or complete molecular orbital calculations including all configuration interaction should lead to the same results if the same approximations have been employed in the two methods. Both hybridization or nonhybridization of xenon $5s$ and $5d$ orbitals with xenon $5p$ orbitals appear to predict correctly a linear structure for XeF_2 and a square planar structure for XeF_4. Papers presented at the Argonne Meeting taking account of xenon $5s$ and $5d$ orbital participation in the bonding of xenon-fluorine compounds were by: Gillespie (*13*) favoring xenon $5s$ and $5d$ orbital participation on the basis of separated electron pair theory; Allen (*14*) suggesting qualitatively that the xenon s and d orbitals should be included; Boudreaux (*15*) implying from his preliminary results that xenon $5p$ participation was probably the important contribution; Hinze and Pitzer (*16*) concluding from their calculations that the principal contribution to the binding came from ionic character arising from xenon $5p$ orbitals and not from xenon $5d$ orbital hybridization—however, stating that changes in that conclusion might result if different approximations were employed in the calculations. Jortner, Wilson, and Rice (*17*), neglecting the participation of xenon $5s$ and $5d$ orbitals, concluded that the properties of XeF_2 and XeF_4 could be satisfactorily explained using only xenon $5p$ orbitals. Lohr and Lipscomb (*18*), taking into account xenon $4d$ orbitals, concluded these $4d$ orbitals were not important in the bonding—this nonparticipation of xenon $4d$ orbitals would have been intuitively expected. It is in the prediction of the molecular structure of XeF_6 where inclusion or noninclusion of xenon $5s$ and $5d$ orbitals could possibly lead to different predictions.

The inclusion of xenon $5d$ orbital hybridization would at first glance seem to indicate for XeF_6 two possible structures, a pentagonal pyramid or an irregular octahedron (both based on fragments of a pentagonal bipyramid in which one vertex is unoccupied). These structures would arise from consideration of the most stable arrangement of seven electron pairs (whether bonded or nonbonded) around a central atom in sp^3d^3 ($sp^3d_\gamma{}^2d_\epsilon$) hybridization (*19*). The arrangement in space of the localized electron pairs (electron pair bonds or unshared electron pairs) is determined by the mutual interaction of all the electron pairs in the valence shell of the central atom. The arrangement of a total of seven bonds and unshared electron pairs is not quite certain since it depends on the form of the interaction potential, whereas the arrangements of two to six electron pairs are independent of the form of the interaction potential (*13*). Following the notation of ligand-field theory, the d_{z^2} and the $d_{x^2-y^2}$ orbitals are referred to as d_γ orbitals and the d_{xy}, d_{xz}, d_{yz} orbitals as d_ϵ orbitals (Fig. 1).

Experimental evidence that it is possible for the d orbitals of an element in this row to participate in bonding can be seen from the structure of iodine heptafluoride (*20*) in which the two geometries found for IF_7 indicate that the iodine atom must be hybridized at least sp^3d^3 (pentagonal bipyramid) or even sp^3d^4 (a configuration derived from dodecahedral eight-coordination).[2]

Xenon $5d$ orbital participation has been invoked successfully to predict the XeF_4 and XeF_2 structures as follows (*5, 7a, 13*):

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This manuscript, originally prepared and submitted for presentation at the Conference on Noble-Gas Compounds held at Argonne National Laboratory, April, 1963, was not presented due to a conflicting lecturing commitment at another conference. It has been modified at the Editor's request to serve as a supplement to the review paper by Dr. H. H. Hyman which appears in this issue, **41,** 174 (1964). Recent references to the IF_7 structures have been added.

[1] It is pertinent to note in regard to this postulated $5d$ orbital participation that in a heavy atom such as xenon, because Russell-Saunders coupling is breaking down, the distinction between p and d orbitals becomes less valid; the d orbitals are also lower than in lighter atoms.

[2] A point which should be noted in the discussion of the bonding in the IF_7 structure derived from dodecahedral eight-coordination is that "there is some residual attraction between the two odd F atoms and distinctly weakened bonding to the central I atom. The molecule dissociates and the extreme fluorinating power of IF_7 may come about from the direct conversion of the odd F atoms into atomic fluorine. Conversely, in the formation of IF_7 from IF_5 and molecular fluorine the configuration of IF_5 requires little rearrangement to achieve the configuration which is stable for IF_7." (*20*)

Postulation of a behavior for XeF_6 analogous to that described above for the isoelectronic IF_7 would seem to have direct pertinence to the experimentally observed anomalous properties of XeF_6 (which may possibly even undergo rapid rearrangement), and would certainly indicate an explanation for the extensive dissociation and extremely rapid fluorine exchange of XeF_6.

In XeF_4 the most stable arrangement of six pairs of electrons around a central atom in sp^3d^2 ($sp^3d_{z^2}d_{x^2-y^2}$) hybridization is at the vertices of an octahedron. One criterion for maximization of stability is minimization of electron repulsions. The largest repulsions are those due to lone-pair–lone-pair interactions; therefore, placement of the two lone-pairs at the top and bottom of the octahedron and the four F atoms in the equitorial plane would lead to maximum stability.

In XeF_2 the most stable arrangement of five pairs of electrons around a central atom in sp^3d($sp^3d_{z^2}$) hybridization is at the vertices of a trigonal bipyramid. Placement of the two F atoms at the apexes of the pyramids would lead to a symmetrical molecule which would be expected to have maximum stability. (There is a delicate balance between lone-pair–lone-pair and bond-pair–lone-pair electron repulsions which permits the linear XeF_2 the minimum electron repulsion.)

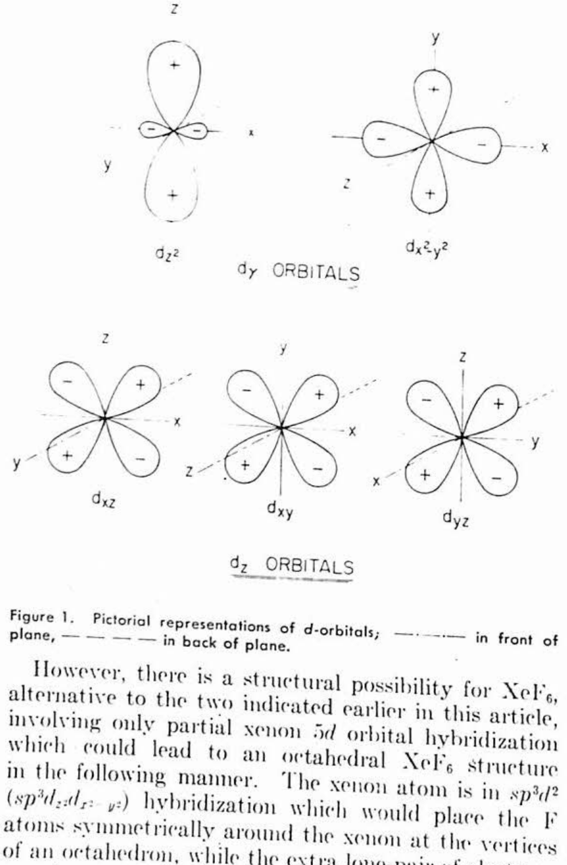

Figure 1. Pictorial representations of d-orbitals; —·—·— in front of plane, — — — — in back of plane.

However, there is a structural possibility for XeF_6, alternative to the two indicated earlier in this article, involving only partial xenon $5d$ orbital hybridization which could lead to an octahedral XeF_6 structure in the following manner. The xenon atom is in sp^3d^2 ($sp^3d_{z^2}d_{x^2-y^2}$) hybridization which would place the F atoms symmetrically around the xenon at the vertices of an octahedron, while the extra lone-pair of electrons remains on the xenon in an unhybridized d_z orbital. This postulate is not without precedent since in a study of the basic factors influencing structural configuration in the stereochemistry of discrete eight-coordinated compounds, unhybridized d orbitals are mentioned as "obviously suitable for housing one or a pair of non-bonding electrons" in certain cases (*21*).

It is crucial to realize when invoking the separated electron pair valence bond method that, under certain special conditions, it is possible to have nonparticipation in valence shell hybridization of d orbitals which contain one or a pair of essentially nonbonding electrons. The valence electron pair bond method is conceptually simple and has found wide applicability in introducing students to chemical concepts. It must merely be used judiciously to preserve its intrinsic value as a basic theoretical tool.

The other theoretical assumption using only the xenon $5p$ orbitals would lead to an octahedral structure for XeF_6.

In conclusion, while a XeF_6 structure based on a pentagonal bipyramidal or distorted octahedral fragment would be conclusive evidence for xenon $5d$ orbital participation, an octahedral XeF_6 structure should not be construed as conclusive evidence favoring either xenon $5d$ orbital participation or the lack of it.

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Principles of Hydrogen Chemistry

Compounds of hydrogen possibly outnumber even those of carbon and are as varied as chemistry itself. Underneath this vast and seemingly heterogeneous array lies the constancy of hydrogen itself, a powerful unifying influence to lend stability and organization to hydrogen chemistry. This constant quality of hydrogen permits the recognition of a set of basic facts and principles, relatively few in number, from which practically all the varied chemistry of this element can be understood. This paper is an attempt to recognize and to summarize these facts and principles, illustrating their meaning, where appropriate, by specific examples.

The hydrogen atom consists of one proton, as a nucleus, and one electron in the first principal quantum level.

The capacity of the first principal quantum level being two, the hydrogen nucleus is not completely shielded by the one electron, and therefore can attract another. This can be accommodated in the single (s) orbital of the first shell. A hydrogen atom can thus form one covalent bond, since it possesses the prerequisite of one outer-shell half-filled orbital.

Formation of one single covalent bond by a hydrogen atom completely uses all of the atom's conventional bonding capacity. It has no additional electrons and no orbital vacancies, after a single covalent bond has been formed. A hydrogen molecule, H_2, in which two atoms have united through such a bond, is therefore inert, being unable to donate, share, or accept electrons. The molecule must be dissociated or, at the least, its bond must first become highly deformed before the hydrogen can react with any other substance. Association among hydrogen molecules is limited to van der Waals interactions, which with only two electrons per molecule are extremely weak, resulting in extremely low melting and boiling temperatures for hydrogen.

Hydrogen is the only element whose atoms have no electrons other than that used for valence. Interactions among all other kinds of atoms are influenced by repulsions among the electron clouds that underly the valence shell, and by shielding of the nuclei by such clouds. Only hydrogen atoms lack these influences.

On the basis that its outer shell is half-filled, hydrogen belongs in the periodic table near other elements (Group IV-A) whose outer shell is half-filled. Hydrogen does not logically belong with the alkali metals, by virtue of their having also one outermost electron per atom, because they exceed it by having six more vacancies. Likewise, it does not belong with the halogens because, unlike them, it does not have three pairs of electrons per atom in the outermost shell, besides the valence electron. Since a hydrogen atom can form but one covalent bond, whereas IV-A elements can form four covalent bonds per atom, hydrogen should actually occupy a separate position in the periodic table. Most logically, however, this should be near to Group IV-A which hydrogen resembles in electronegativity.

Hydrogen has an electronegativity only slightly above the median. It can therefore act as oxidizing agent toward less electronegative elements, and as reducing agent toward more electronegative elements. The order of increasing electronegativity is: Cs, Rb, K, Na, Li, Ba, Sr, Ca, Mg, Be, Al, Cd, Si, B, Zn, In, Hg, Tl, Pb, Sn, Bi, P, Sb, H, Ge, Te, C, I, As, S, Se, N, Br, Cl, O, and F. Toward any of the elements to the left of hydrogen, it acts as oxidizing agent. Toward any of the elements to the right of hydrogen, it acts as reducing agent.

Hydrogen forms conventional binary compounds only with the rare-gas-shell and 18-shell type elements. It forms compounds with each of these. These compounds have the composition expected from the capacity of each atom to form conventional single covalent bonds. Their type formulas for each major group of the periodic table are: I-A, EH; II-A, EH_2; III-A, EH_3, IV-A, EH_4, V-A EH_3; VI-A EH_2; and VII-A, EH.

The strength of covalent bonds to hydrogen appears to be greatest for atoms that are relatively small and to decrease with increasing size (principal quantum number of the valence shell) of the other atom. The most stable binary hydrogen compounds are those of carbon, nitrogen, oxygen, and fluorine. Within each major group of the periodic table, the stability tends to diminish with increasing size of the atom joined to hydrogen. Hydrogen compounds of mercury, thallium, lead, and bismuth are so unstable that knowledge of them is scant. Hydrogen telluride is least stable in its group (possibly excepting polonium hydride), and hydrogen iodide is least stable in its group (possibly excepting hydrogen astatide).

When hydrogen acts as an oxidizing agent, it acquires partial negative charge. In proportion to the amount of this charge, hydrogen compounds tend to become associated, with consequent reduction of volatility and increase in melting point. The table lists the binary compounds of hydrogen in order of decreasing negative and increasing positive partial charge.

The hydrides of the alkali and alkaline earth metals, for example, form ionic crystalline lattices, most of which remain solid and nonvolatile to fairly high temperatures, when they decompose before melting. Hydrides of other elements less electronegative than hydrogen, in which the bonds are not as polar as in the salt-like hydrides, appear to become associated through hydridic bridging, in which hydrogen atoms bridge two molecular units. This may extend to highly polymeric solids, as in BeH_2, MgH_2, AlH_3, InH_3, or it may result merely in the formation of volatile dimers, such as B_2H_6 and possibly Ga_2H_6.

Estimated Partial Charge on Combined Hydrogen
(in electrons)

Negative		Nearly neutral		Positive	
CsH	−0.59	SnH_4	−0.02	HI	0.04
RbH	−0.58	GeH_4	−0.01	H_2S	0.05
KH	−0.58	PH_3	−0.01	H_2Se	0.06
NaH	−0.50	SbH_3	−0.01	NH_3	0.06
LiH	−0.50	CH_4	0.01	HBr	0.12
BaH_2	−0.33	H_2Te	0.01	H_2O	0.12
SrH_2	−0.31	AsH_3	0.02	HCl	0.16
CaH_2	−0.29			HF	0.25
MgH_2	−0.18				
BeH_2	−0.13				
AlH_3	−0.12				
CdH_2	−0.09				
ZnH_2	−0.06				
B_2H_6	−0.05				
InH_3	−0.05				
SiH_4	−0.05				

When conventional covalence would result in binary hydrogen compound molecules having one or more outer-shell vacant orbitals and the hydrogen bears partial negative charge insufficient to form an ionic lattice, these orbitals tend to share the electrons of the hydrogen atoms of other molecules, resulting in an association of the molecules through hydridic bridging. The most familiar example of hydridic bridging occurs in diborane, B_2H_6. Each boron atom has four outer orbitals but only three outer electrons. When it has joined to three hydrogen atoms by conventional covalent bonds, then it still possesses an outer vacant orbital. In the presence of some electron donor, this orbital quickly becomes occupied through formation of a molecular addition compound, such as $BH_3{:}N(CH_3)_3$. When only BH_3 groups would be present, however, they pair completely. One hydrogen atom of each BH_3 appears to lend the pair of bonding electrons to the other boron in its otherwise unoccupied orbital. Thus is formed a three-center bond, in which one pair of electrons holds two boron atoms to the same hydrogen through one orbital from each boron and one on the hydrogen. Two such three-center bonds appear to comprise the hydridic bridging in diborane. Such hydrogen bridging is called "hydridic" because negative charge on hydrogen seems to be required. Similar situations in which the hydrogen is not partially negative, such as $BClH_2$ (partial charge on H, 0.03), do not exhibit the dimerization characteristic of diborane.

In proportion to the amount of its negative charge, hydrogen loses oxidizing power and acquires reducing power in the compound and tends to gain electron donating ability. All compounds in which hydrogen is negatively charged tend to be active reducing agents, although the relative potential reducing power may be obscured by differences in reaction mechanism. Even water is an effective oxidizing agent, with its positive hydrogen; and most compounds of negative hydrogen are readily hydrolyzed, with the liberation of molecular hydrogen formed by uniting negative hydrogen with a proton. Highly negative hydrogen can become a hydride ion ligand, contributing a pair of electrons to an available orbital of another atom. For example, it can join with a BH_3 group to form the borohydride ion, BH_4^-, or with an AlH_3 group to form the aluminohydride ion, AlH_4^-. To act as ligand, the hydrogen apparently must have a higher negative charge than the hydrogen atoms already attached to the boron or aluminum.

When hydrogen acts as a reducing agent, it acquires partial positive charge. In proportion to the amount of this positive charge, hydrogen gains oxidizing power and loses reducing power in the compound and, as a releasable proton, tends to gain electron accepting ability or, in other words, becomes acidic. All compounds of hydrogen in which the hydrogen has partial positive charge are at least potentially oxidizing and acidic; they tend to be more so, the more positive the charge. However, the most important factor, in any reaction involving the release of a proton from a hydrogen compound, is the electron-donating capacity of the negative ion that would remain. The transfer of a proton is a competitive process, essentially between an electron pair on each of two atoms. The relative availability of each electron pair to the proton determines the extent of transfer, if any. Therefore, although the hydrogen tends to be more protonic, the higher its positive charge, a high charge is not necessarily a criterion for high acidity under all conditions. For example, in the hydrogen halides, the acidity of aqueous solutions increases from hydrofluoric acid, which is weak, to hydriodic acid which is very strong. (Aqueous hydrochloric and hydrobromic acids are also strong, but in more acidic solvents than water the distinction can be made that HI is stronger than HBr which in turn is stronger than HCl.) Bond polarity is in the opposite order, the highest positive charge on hydrogen occurring in HF, and in HI the hydrogen is only slightly positive. The difference here lies in the capacity of the halide ion in water to donate an electron pair to a proton. The fluoride ion does this so effectively that HF is a weak acid. The iodide ion does this poorly, as do also chloride and bromide ions, making HCl, HBr, and HI strong acids. An explanation is suggested below.

Positive hydrogen, of course, is important not just in water solutions for it possesses oxidizing power in the compounds separate from water. Such compounds can, for example, remove electrons from metals and react with compounds of negative hydrogen, releasing molecular hydrogen gas, or with compounds of negative alkyl, releasing the corresponding alkane.

Positively charged hydrogen can become attracted to an electron pair on another molecule (or on another atom of the same molecule) electrostatically, with sufficient force to form a weak bond, called a "protonic bridge," holding the molecules together. This is what is commonly called a "hydrogen bond." The term "protonic bridge" seems preferable to indicate that positive charge on the hydrogen is necessary and to distinguish it from the different type of hydrogen bonding called "hydridic" bridging. Protonic bridging is a property exclusively of hydrogen, because of the absence of electrons underlying the valence shell, in hydrogen alone. When the valence electrons are partially withdrawn from the hydrogen, the nucleus becomes somewhat exposed on the far side of the bond and can exert an electrostatic attraction for an electron pair of another atom if that pair is sufficiently available. In order to be available, the atom on which the pair resides must have partial negative charge, and it must be small. The requirement of negative charge means that the electrons are more easily available, being farther removed from their own atomic nucleus and that any repulsive effect of that nucleus toward the positive hydrogen is effectively shielded. The requirement of small size seems to suggest that in larger atoms, even when they bear partial negative charge, the electron pairs are not concentrated within so small a space as in the small atoms and hence not so available to a proton of another molecule. These requirements practically restrict the effectiveness of protonic bridging to compounds in which nitrogen, oxygen, and fluorine bear partial negative charge and are available to positively charged hydrogen. The hydrogen is usually attached to one of these elements, too, but may be attached to some other element such as carbon as long as the hydrogen bears substantial positive charge.

The physical properties of ammonia, water, and hydrogen fluoride that reflect the state of aggregation of the molecules, such as melting and boiling points, give ample evidence of protonic bridging in these compounds. The essential absence of such bridging in their congeners is similarly shown by their much lower boiling and melting points, despite their greater molecular weight.

Compounds in which the hydrogen is neither appreciably positive nor appreciably negative show no evidence of association through either protonic or hydridic bridging and tend, therefore, to be low-melting and volatile. Only a few elements are close to hydrogen in electronegativity, and therefore compounds of relatively uncharged hydrogen are restricted to these. They include all hydrocarbons as well as methane, germanium hydrogen compounds, phosphine PH_3, arsine AsH_3, and stibine SbH_3, and hydrogen telluride also.

Compounds in which hydrogen is close to neutral also are relatively inert chemically at ordinary temperatures, being not easily oxidized or reduced and neither acidic nor basic. Methane and germane, for example, although they will burn in air when ignited, are not spontaneously inflammable as are many compounds of negative hydrogen, and they are inert toward hydrolysis. They are neither acidic nor basic.

Hydrogen and carbon are the only two elements whose atoms, when they have formed all the covalent bonds of which they are capable, have neither outermost vacancies nor outermost electron pairs available for further reaction. This is highly significant, accounting for the relative unreactivity of the alkanes and of alkyl groups throughout organic chemistry. Such molecules and groups are relatively invulnerable to chemical attack, which commonly requires the initial formation of unstable intermediates through the use of unshared pairs of orbital vacancies. Outer *d* orbitals, not present in carbon, are available in all other elements of this group, imparting higher reactivity to their compounds.

The small size of carbon permits strong bonds to hydrogen, and the similarity in electronegativity prevents appreciable bond polarity in hydrocarbons. These facts contribute greatly to the importance of hydrocarbon chemistry, for they permit indefinitely extensive joining together of carbon atoms when the remaining bonds are to hydrogen. The "uniqueness" of organic chemistry is not the result of some highly special quality of carbon, as is often implied, but rather, the resultant of a particular combination of qualities and circumstances, none unusual by itself. In summary, these include: the small radius of carbon so that its bonds to hydrogen are stable; the electronegativity similarity between carbon and hydrogen; the unavailability of orbital vacancies or unshared electron pairs on either carbon or hydrogen when attached by single covalent bonds; the ability of carbon to form multiple bonds using its *p* orbitals; and the tetravalence of carbon.

Transition metals absorb hydrogen to a widely variable degree, forming interstitial compounds of stoichiometry depending on conditions and having properties sometimes resembling but generally unlike those of the major group hydrogen compounds. For example, in scandium, yttrium, and some of the inner transition elements including plutonium, MH_2 phases appear to occur in which, however, the composition tends to be more nearly $MH_{1.8}$. Additional hydrogen can be dissolved in these phases. An MH_3 phase occurs in a few. The MH_2 phases are hydrolyzed by water and acids; the hydride of Ti, however, appears unaffected by water. In general the most tightly associated of the transition metals (those having *d* orbitals nearly half full) appear least reactive toward hydrogen.

Metal-hydrogen bonds are found in a number of complex molecules or ions. Metals that may be so involved include Ti, V, Cr, Mn, Mn, Fe, Co, Ni, Mo, Tc, Ru, Rh, Pd, Ta, W, Re, Os, Ir, Pt. Although these complexes might be regarded as examples of hydride ion acting as ligand, the hydridic character if any is not necessarily evident. For example, although such complexes appear to be quite susceptible to oxidation, they resist hydrolysis and some tend to act as acids in water solution. Others, however, are basic. The nature of these complexes remains to be clarified.

In summary, the chemistry of hydrogen depends largely on the fundamental nature of hydrogen atoms. Application of the principle of electronegativity equalization to the estimation of the condition of combined hydrogen with respect to charge leads to recognition of a consistent pattern of behavior of hydrogen compounds, from which useful principles such as those listed here may be derived. In this sense it is possible for teachers to present the chemistry of hydrogen as a self-consistent, logical unit upon which a practical understanding can be based.

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Principles of Oxide Chemistry

The purpose of this article is to summarize the very extensive and varied oxide chemistry of oxygen by means of a self-consistent set of statements and principles applicable to the whole area. It is hoped that such a summary may prove useful to students eager to consolidate their learning, and to professional chemists for whom, as for most of us, the comprehensive view becomes increasingly clogged with masses of detail or increasingly nebulous through preoccupation with other specializations. In general form, this article follows earlier papers of this series.[1]

Bonding

Oxygen atoms can form two single covalent bonds or one multiple bond, ordinarily a double bond. These abilities depend on the electronic structure of the oxygen atom, which has a closed first shell of two electrons and a second and outermost shell having six electrons in the four *s* and *p* orbitals. These electrons, in agreement with the Hund rule of maximum multiplicity, are spread out as far as possible among the four orbitals, and therefore although of necessity paired in two orbitals, occupy the other two singly: $1s^2$, $2s^2$, $2p_x^2$, $2p_y$, $2p_z$. The two half-filled orbitals are the requisites for either two single covalent bonds or one double bond.

When an oxygen atom forms two single covalent bonds, the angle between these two bonds is influenced by the presence of the two unshared electron pairs also on the oxygen. This bond angle may variously be accounted for in terms of hybridization (*s* character) of the bonds or coulombic repulsions among the four electron pairs, in either explanation modified by the nature of the attached groups. For example, complete hybridization of the unshared pair orbitals with the bonding orbitals would lead to the familiar tetrahedral configuration associated with sp^3 hybridization. The bond angles thus resulting, 109°28′, would be exactly the same if they were the simple consequence of coulombic repulsions among the four electron pairs, causing them to become distributed as far apart on the atomic sphere as possible. However, the tetrahedral angle would be expected to be modified if hybridization were less complete, or in consequence of steric or coulombic interactions between the two atoms bonded to the oxygen. Furthermore, in the coulombic interpretation, two unshared pairs of electrons would be expected to have greater repulsions than two bonding pairs since the former would be localized exclusively on the oxygen. They would therefore tend to force one another somewhat farther apart and the bonding pairs somewhat closer together, diminishing the bond angle. One would also expect that polarity of the covalent bonds could influence the bond angle slightly, partial monopolization of the bonding electrons by the oxygen causing them to resemble the unshared electron pairs in repulsive effects. But in practically all compounds for which the angle between two single covalent bonds to oxygen is known, the angle is somewhere within the limits of 100 to 111°. Some representative examples are shown in Table 1. Notice, however, the principle below discussing the use of unshared pairs.

Table 1. Typical Angles between Two Single Bonds to Oxygen (in degrees)

H_2O	104.5	$(CH_3)_2O$	111
F_2O	103.2	CH_3OH	106-110
Cl_2O	110.8	$FONO_2$	105

An oxygen atom can act as electron acceptor, joining to another atom through a coordinate covalent bond. Such action depends on the absorption of a relatively small amount of "pairing" energy by the oxygen so that one of the single electrons pairs with the other, leaving its original orbital completely unoccupied. The acceptor action of oxygen seems, however, relatively rare, being confined to its uniting with nitrogen in the amine oxides, such as $(CH_3)_3N{:}O$. In all seemingly analogous compounds, such as the corresponding oxides of phosphorus, the bonds to oxygen are significantly shorter than expected for single bonds, indicating a double bond formation through utilization of the outer *d* orbitals on the phosphorus or other atom. Presumably such double bonding occurs wherever possible. The common representations of such aggregates as sulfate, phosphate, and perchlorate ions as though they consist either of coordinate covalent single bonds or of "resonance structures" including single bonds are inconsistent with the bond lengths and the general behavior of oxygen.

Oxygen when combined through two single covalent bonds seems able under certain circumstances to utilize its "unshared" pairs of electrons in the two bonds at least to some extent. This is suggested by bond angles in silicates and polyphosphates, for example, which are much larger than 109°. Some examples are given in Table 2. Notice that in one compound, the bond angle is 180°, the maximum that would be expected from two bonds if they involved all the external electrons of the oxygen atom. Bond angles between 109 and 180° are believed to represent a condition of partial double bonding, in which the outer *d* orbitals (or *s*-*p* orbitals if available) are able to acquire the extra electron pairs of the adjacent oxygen atom only incompletely.

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[1] SANDERSON, R. T., J. CHEM. EDUC., (*a*) **38**, 32 (1961); (*b*) **41**, 13 (1964); (*c*) **41**, 331 (1964); (*d*) **41**, 361 (1964).

Table 2. Some Examples of Angles between Two Partially Multiple Bonds to Oxygen (in degrees)

POP in ZrP_2O_7	180	SiOSi in Na_2SiO_3	137.5
POP in P_4O_6	128	BOB in $Co_2B_2O_5$	140
AsOAs in As_4O_6	127	SeOSe in SeO_2	125
SiOSi in Si_2Cl_6O	130	SiOSi in SiO_2	142

Oxygen when combined through two single covalent bonds or by a double bond has two additional pairs of electrons that may permit the combined oxygen to act as electron donor to a third atom. Usually only one pair is donated at a time. Hundreds or thousands of compounds are known in which combined oxygen forms addition compounds or complex ions through donation of an electron pair by the oxygen atom. A typical addition compound is that of BF_3 and dimethylether, $F_3B:O(CH_3)_2$. Elements which form complexes chiefly with donor oxygen are found mainly in major groups III-A, IV-A, V-A, VI-A, and VII-A. In addition, oxygen complexes are formed by lithium and sodium, all the II-A metals, and the transition elements from III-B through VII-B, as well as iron.[2]

Under special conditions, oxygen appears to form bonds of higher order than 2, up to 3. Familiar examples are nitric oxide and carbon monoxide. The former can be represented as involving single electron resonance and thus having a bond order of 2.5. The latter can be accounted for if one electron is transferred from the oxygen to the carbon, leaving each with an electronic configuration resembling that of a nitrogen atom, and permitting formation of a triple bond between the two atoms resembling the very stable triple bond of the nitrogen molecule:

$$:\overset{-}{C}\equiv\overset{+}{O}:$$

When electrons are exceptionally easily available to it, as from the alkali metals of higher atomic weight, molecular oxygen can acquire them without first dissociating. The major product of burning sodium in air is the peroxide, Na_2O_2, and potassium, rubidium, and cesium under similar conditions form superoxides, MO_2. The oxygen atoms in the crystalline aggregates of these compounds are paired and may be regarded as $O_2^{=}$ and O_2^{-} ions.

With the exception of fluorine, oxygen is most electronegative of all the elements. Its bonds to all other elements are therefore polar, with oxygen relatively negative. Naturally, the most polar bonds to oxygen will be those of the least electronegative elements, the alkali and alkaline earth metals. The least polar bonds will be those of the other highly electronegative elements, chlorine, nitrogen, sulfur, etc., with oxygen.

Physical Properties

If in the simplest oxide molecule that might form under ordinary conditions, any low energy orbitals on the other element are left empty and uninvolved in the bonding, the oxide will invariably condense to larger aggregates, presumably making fullest possible use of the otherwise vacant orbitals. This is an example of the general tendency for chemical combination to continue if possible until all available low-energy orbitals are utilized, in one way or another, in the bonding.[1a] Such compounds as Na_2O, CaO, and Al_2O_3 therefore exist as highly condensed aggregates rather than individual molecules.

If in the simplest oxide molecule that might form, all available outer orbitals are occupied, the compound often remains molecular, larger aggregates forming, if at all, only through relatively weak van der Waals interactions. Examples are CO_2, SO_2, P_4O_{10}, and Cl_2O_7 in which no outer orbitals of low energy remain vacant.

Even when they lack outer vacant orbitals, simple molecules may become giant polymers if they have double bonds that are less stable than two single bonds. This effect increases with diminishing availability of p orbitals for double bonding, increasing strengthening of single bonds to oxygen through d π-bonding, and increasing bond polarity. Simple molecules such as SiO_2, SeO_2, and TeO_2 do not represent the compounds as they exist under normal conditions, for these substances are highly polymeric. When faced with such problems as why CO_2 is monomeric and SiO_2 is polymeric, we need to recognize three factors First, only the elements carbon, nitrogen, and oxygen appear to form double bonds easily using only *s* and *p* orbitals. Addition of another principal quantum shell seems to inhibit the closeness of interaction required for this kind of multiplicity. Other elements may join to these by multiple bonds but not so easily using *p* orbitals. Second, when outer *d* orbitals are available, these may become utilized in multiple bonding. This may permit ordinary double bonding to oxygen, as in the phosphine oxides, $R_3P{=}O$, or reinforcement of the single bonds to oxygen, as in SiO_2, so that they are more stable through use of the otherwise unshared pairs on oxygen. Third, the more polar the bond, the more likely is polymerization, rather than simple double bonding. In the example given, SiO_2 is polymeric although CO_2 is not because silicon is less able to form *p* π-bonds to oxygen than is carbon, silicon can use outer *d* orbitals not available in carbon, for reinforcing its "single" bonds to oxygen, and silicon is less electronegative than carbon and therefore silicon-oxygen bonds are more polar.

Crossing the periodic table from center to right, in the area of no vacant outer orbitals except *d* type, one can observe the effects of decreasing bond polarity in the oxides. Silicates are highly polymeric, phosphates also but less stably so, and sulfur dioxide and sulfur trioxide either not at all (SO_2) or only weakly (SO_3), whereas the chlorine oxides are all simple molecular species.

The state of aggregation of an oxide depends partly on the charge on oxygen, the coordination number of the oxygen tending to be higher, the higher its negative charge. Evidence of this is given in Table 3. It will be observed that the coordination number of oxygen in its major group oxides is roughly one for each tenth of an electron acquired by the oxygen. In the transition metal oxides, whose metal atoms are generally more effective acceptors, a lower negative charge on oxygen seems adequate, as shown in Table 4. The data here are only very approximate, however, because of uncertainties as to the electronegativities, and therefore partial charges, of the transition elements. The possible significance of this relationship is discussed under the following principle.

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[2] BAILAR, J. C., Editor, "Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, 1956.

The solid oxides, which are nonmolecular because the simple molecules would have vacant outer orbitals, including even those conventionally described as "ionic," are probably more accurately described as "coordination polymers." The argument developed here is that recently proposed.[3] The concept of "ionic" oxides requires that oxygen atoms remove electrons completely from metal atoms, forming $O^=$ ions and metal cations. Since both types of ions must always be formed endothermically, the necessary requirement of energy is rationalized by the conventional explanation that it is more than adequately supplied as electrostatic energy evolved when the oppositely charged ions come together in the crystal. But this explanation ignores the vital facts that positive ions have a strong attraction for *electrons* (not the whole negative ion) and that negative ions are able to supply electrons. It is incredible, for example, that an oxide ion, which could lose its two extra electrons with a net gain of about 168 kcal per mole, would sit unaffected completely surrounded at close range by six calcium ions, each of which could acquire two electrons with a net gain of about 415 kcal per mole. It is equally incredible that a calcium ion could sit completely surrounded by six such oxide ions without affecting them. Surely the valence electrons must be *shared* between the two elements under such conditions, for they cannot conceivably be monopolized by one.

Table 3. Coordination Number and Charge of Oxygen in Some Major Group Oxides

	Charge on O	C. N.		Charge on O	C. N.
Cs_2O	−0.96	8	CaO	−0.57	6
Rb_2O	−0.92	8	MgO	−0.42	6
K_2O	−0.89	8	BeO	−0.35	4
Na_2O	−0.81	8	Al_2O_3	−0.31	4
Li_2O	−0.80	8	B_2O_3	−0.24	2
BaO	−0.67	6	SiO_2	−0.23	2
SrO	−0.62	6	Co_2	−0.11	2

Table 4. Coordination Number and Approximate Charge of Oxygen in Some 18-Shell and Transition Metal Oxides

	Approx. Charge on O	C. N.		Approx. Charge on O	C. N.
Cu_2O	−0.45	4	NbO_2	−0.30	4
TiO	−0.37	6	ZnO	−0.29	4
FeO	−0.35	6	Fe_2O_3	−0.25	4
CdO	−0.32	6	SnO	−0.25	4
Ti_2O_3	−0.31	4	PbO	−0.25	4
ZrO_2	−0.30	4	TiO_2	−0.25	3
			VO_2	−0.25	3

To understand the nature of this sharing, we must recognize that in any condensed system such as represented by CaO, an oxygen atom has not two valence electrons but six, and the calcium atom, with two valence electrons, has not two valence orbitals but at least four. We may therefore picture CaO as composed of a symmetrical (cubic) aggregate of calcium and oxygen atoms mutually sharing eight electrons per atom pair. If we assume that these elements share these electrons unevenly as determined by their initial electronegativities, and that the principle of electronegativity equalization is applicable, then we can interpret the calculated partial charges of 0.57 on calcium and −0.57 on oxygen to mean that on the average, an oxygen atom holds 6.57 or 82% of the eight valence electrons leaving 1.43 or 18% to the calcium.

To be rationalized next is the 6:6 coordination in CaO if the bonds are coordinate and yet only eight electrons and four orbitals per atom are involved. The relatively high negative charge on oxygen makes it a very good potential donor. It can evidently form a more stable aggregate by grouping more acceptors on a "part-bond" basis than by restricting the number of acceptors to the number of electron pairs available. Similarly, the calcium can evidently serve more effectively as partial acceptor to more donors than as full acceptor to fewer donors. In other words, a kind of coordination resonance may be imagined, in which six bonds of order 0.67 impart greater stability than would four single bonds.

Why should such partial bonding give greater stability? This is not altogether different from the situation in metals. As a general principle,[1a] partial sharing of electrons among many orbitals and atoms is energetically more favorable than full sharing between fewer orbitals and atoms, presumably for the following reason: When outside electrons are attracted to an atomic nucleus and become increasingly closely associated with it, the interelectronic repulsions increase more rapidly than does the nuclear attraction. The initial partial gain of electrons is therefore proportionately more exothermic than the subsequent complete gain.

When the charge on oxygen is too low to permit a coordination number larger than the number of available atomic orbitals, then conventional coordination bonds of the localized electron pair type can and do form. For example, in ZnO where the charge on oxygen is estimated as −0.29, each zinc atom is joined at the corners of a tetrahedron to four oxygen atoms and each oxygen atom is similarly joined to four zinc atoms. The solid structure thus consists of a giant three-dimensional network polymer.

The transition metal oxides differ from the major group oxides by the utilization of underlying *d* orbitals which tend to offer greater variety and strength of bonding. They also appear to exhibit a greater variety of compositions, in which deviations from the conventional stoichiometries are common. Here too, nevertheless, their description as "coordination polymers" seems superior to their usual designation as ionic solids.

The physical properties of oxides depend only indirectly on the nature of the simplest possible formula unit, but directly on the state of aggregation. If the oxide is of simple molecules, there may be slight dipole-dipole interactions but these cannot be great because the bonds are not very polar, as proved by the fact that the oxide is molecular. The chief interactions will then be van der Waals attractions and inter-cloud repulsions, the result being, ordinarily, very low melting and boiling points and relatively high volatility. The crystalline state is expected to be soft. Since intermolecular distances are in such compounds substantially greater than bond lengths, the compounds would also be expected to be relatively low in density.

Polymeric or "giant molecule" oxides cannot change phase on heating without the breaking of relatively strong polar covalent bonds. They therefore tend to be high melting, relatively nonvolatile substances, and fairly hard. This refers to oxides joined together by relatively localized covalent bonding. No clear line of distinction can be drawn between such compounds and those in which the coordination number of oxygen exceeds 2, for the range from "covalent" to "coordination polymers" and/or "ionic" bonding can be very gradual. In general, however, these states of aggregation have in common high bonding strength, with consequent high melting points and low volatility. Table 5 lists typical examples both of relatively nonpolar and relatively polar oxides, together with some of their properties.

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[3] SANDERSON, R. T., *Inorg. Chem.*, in press.

Table 5. Partial Charge on Oxygen and Properties of Some Typical Oxides

Compound	Charge on O	$\Delta H_f°$/equiv.	mp
Na_2O	−0.81	−49.7	920
CaO	−0.57	−75.9	2587
MgO	−0.42	−71.9	2802
Al_2O_3	−0.31	−65.3	2027
ZnO	−0.29	−41.6	1975
B_2O_3	−0.24	−50.3	450
SiO_2	−0.23	−51.3	1700
SnO_2	−0.17	−34.7	1927
P_4O_{10}	−0.13	−36.0	422
CO_2	−0.11	−23.5	−56.6
SO_3	−0.06	−15.9	(γ)16.9
SeO_3	−0.06	...	118
N_2O_5	−0.05	−1.0	30
Cl_2O_7	−0.01	4.5	−81.5

Chemical Properties

The ability of oxides to act as oxidizing agents tends to be highest for those with least polar, and consequently least stable, bonds and to diminish with increasing partial negative charge on the combined oxygen. The oxidizing powers of such compounds as oxides of chlorine, oxides of nitrogen, sulfur trioxide, and the highest oxides of some of the transition elements, such as CrO_3 and Mn_2O_7, are well known. On the other hand, oxides in which the partial charge on oxygen is relatively high have no oxidizing power except under extreme conditions, such as those under which magnesium oxide oxidizes ferrosilicon in the commercial production of metallic magnesium. This quality of combined oxygen stems from the greater stability associated with bond polarity, such that oxygen tends to leave a compound in which it is only slightly negative to form a new combination in which it is more negative. Stated differently, the oxygen does not lose much of its electronegativity in combining with other elements of high electronegativity or when competing with several other oxygens or other highly electronegative atoms for a very limited supply of electrons. It retains its electronegativity and therefore oxidizing power in the compound. But in combination with elements that supply it with relatively high negative charge, oxygen retains little or no electronegativity and thus no appreciable oxidizing power. Bonds of oxygen to larger atoms such as gold, mercury, thallium, lead, and bismuth may be unstable regardless of polarity and if so, the oxides will naturally have good oxidizing powers as sources of free oxygen.

One of the most misleading aspects of the conventional use of oxidation numbers is the ascribing of oxidizing power exclusively to a high positive oxidation state in compounds that include such a state. The oxidizing power of CrO_3, for example, is said to be the result of the presence of Cr^{6+}, and the oxygens are all assigned the oxidation number of −2. In fact the oxygens can bear only slight negative charge in this compound and its oxidizing power can much better be described as resulting from both elements, but principally the oxygen. In any reaction in which CrO_3 acts as oxidizing agent, the chromium becomes less positive and the oxygen becomes more negative. The chromium atom, which in CrO_3 probably does not even remotely resemble a Cr^{6+} ion, is just as electronegative as the oxygen, in the compound, if the principle of electronegativity equalization is applicable. However the chromium has little attraction for any electrons beyond its own so it is reasonable to ascribe the oxidizing power primarily to the oxygen.

Similarly, the oxidation of sodium metal by water is thought of, in terms of oxidation number, as simply the reduction of positive hydrogen by the sodium, the hydrogen thus being the oxidizing agent. In fact, however, both the hydrogen and the oxygen in the hydroxide ion must have much greater control of electrons than they did in the water. Oxygen bears a partial negative charge of −0.25 in water but in hydroxide ion the charge is −0.67. Clearly it is not realistic to regard that hydrogen which becomes molecular hydrogen in the reaction with sodium as the sole oxidizing agent. The true agent is water.

The principal fundamental characteristic of acidic oxides is low negative charge on oxygen. Without detailing the numerous varying acid-base concepts, we can think of acids or acidic oxides as characteristically being electron attractors and acceptors. We then need to understand what low negative charge on oxygen has to do with acceptor properties. Combined oxygen itself cannot act as acceptor, for it possesses no available vacant orbital. But low negative charge on oxygen means that the oxygen is attached to one or more highly electronegative atoms, which effectively resist electron removal by the oxygen. These atoms may be electronegative for one or both of two reasons. They may be atoms of highly electronegative elements or they may be atoms of elements relatively low in electronegativity but caused to become highly electronegative through electron withdrawal by several competitive highly electronegative atoms. In either case, the other element, unless it is fluorine, is caused by the action of the oxygen to become more electronegative than it was; and it also has orbitals that can become acceptors. The acceptor properties of an orbital are improved by withdrawal of electrons even slightly, and outer *d* orbitals become more stable as an atom acquires partial positive charge. On the other hand, if the charge on oxygen is relatively high, this corresponds to low electronegativity in the compound. The other element, to the extent that it can act as acceptor, can be fully satisfied by its own oxygen as donor.

The principal fundamental characteristic of basic oxides is high negative charge on oxygen. The reason for this is that the quality of basicity arises from the availability of electron pairs. Oxygen has two such pairs, but they do not become available until the oxygen has acquired partial negative charge. Some typical oxides, both basic and acidic, are listed in Table 6 together with their partial charge on oxygen.

Neutralization of an acidic oxide by a basic oxide is essentially the acceptance by the acidic oxide of the basic oxygen as donor. The bond usually becomes multiple rather than remain simple coordinate, however. For example, the reaction between CaO and SO_3 involves acceptance of the partially negative oxygen from CaO by the SO_3, but the S—O bonds in the sulfate group have apparently a bond order close to or equal to 2.

Table 6. Partial Charge on Oxygen and Acid-Base Properties of Some Oxides

S = strong, M = medium, W = weak; A = acid, B = base, AB = amphoteric

Compound	Charge on O	Acid-base
Na_2O	−0.81	SB
Li_2O	−0.80	SB
MgO	−0.42	WB
BeO	−0.35	AB
Al_2O_3	−0.31	AB
B_2O_3	−0.24	WA
SiO_2	−0.23	WA
P_4O_{10}	−0.13	MA
CO_2	−0.11	WA
SO_3	−0.06	SA
N_2O_5	−0.05	SA
Cl_2O_7	−0.01	SA

The action of water on oxides, whenever definite compounds other than simple hydrates are formed, is the reaction between an acidic and a basic oxide. Water itself, like other oxides in which the negative partial charge on oxygen is of intermediate magnitude, may act as acceptor (acid) or donor (base), as determined by the condition of oxygen on the other oxide. It may act as acceptor through its protons:

$$CaO + H_2O \rightarrow (Ca{-}OH^+ + OH^-)$$
$$(CaOH^+ + OH^-) \rightarrow Ca(OH)_2$$

Or, it may act as donor through its oxygen:

$$SO_3 + H_2O \rightarrow H_2O{:}SO_3 \rightarrow H_2SO_4$$

The electron donating ability of oxygen increases with increasing negative charge. Oxides whose oxygen is most negative are most strongly basic, e.g., the alkali metal oxides. In oxyanions, as will be discussed presently, a higher negative charge on oxygen means better donation to a proton and better coordination bonding in general.

The electron donating ability of negative oxygen is better when the oxygen is attached by single bonds than when there is bond multiplicity. Presumably this is the result of greater localization of an electron pair on oxygen when its electrons are spread out to four general locations rather than tending to concentrate in three. If, for example, oxygen is attached to but one other atom, as in a ketone or an oxyanion such as sulfate, using two of its electrons and orbitals for the bonding, the entire atom away from the bond is available for the two nonbonding electron pairs. These evidently spread out so that they are less available for sharing with another atom, especially with a proton. But if the oxygen is joined by single bonds to two other atoms, as in H_2O, or by one single bond as in OH^- ion, the space per electron pair is more limited and the donating ability is improved.

The relative strengths of aqueous oxygen acids can be partly understood in terms of the negative charge on oxygen and the relative extent of localization of the electron pairs for donation. The acid dissociation of a hydrogen compound in water may usefully be regarded as a competition between water molecules and anions of the acid, each acting as electron donor to a proton:

$$HA + H_2O \rightleftharpoons A^- + H^+ + H_2O \rightleftharpoons A^- + H_3O^+$$

We may compare water molecules with the anions, with respect to their ability to provide an electron pair to a proton. When the acid under consideration is a hydroxy acid, the donor in each case is oxygen. The difference in donor ability is the result of a difference in the condition of the combined oxygen in water and anion.

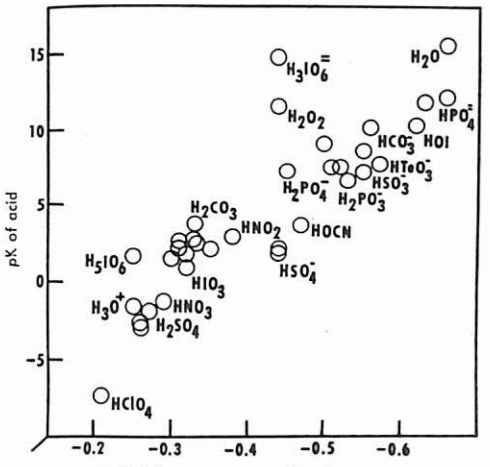

Figure 1. Relation of acid strength to partial charge on oxygen in oxyanion. (Points unlabeled represent the following acids with their; pK values: $HSiO_3^-$, 12; HBO_2, 9.2; HOBr, 8.7; HOCl, 7.6; $HSeO_4^-$, 2.1; H_2SeO_3, 2.6; H_2TeO_3, 2.5; $HClO_2$, 2.0; H_3PO_3, 2.0; H_2SO_3, 1.8; H_3PO_4 2.1 $H_2S_2O_3$, 0.6.)

The principal factor contributing to the donor ability of combined oxygen is its electron supply, which can be measured as partial charge. The higher the negative charge on oxygen, the better able it is to contribute an electron pair to coordinate a proton. On this basis we may expect a rough correlation between acid strength and the partial charge on oxygen in the anion. The lower this charge, the less able is the anion to compete with water and therefore the stronger the acid. The extent of this correlation is indicated in Figure 1. Although other factors obviously cloud the picture, one may observe that strong oxyacids in general have a partial charge on oxygen in their anion less than −0.3, anions of moderately weak oxyacids tend to have a partial charge on oxygen greater than −0.3 but less than about −0.5, and most acids are very weak which yield anions in which the charge on oxygen is greater than −0.5.[4]

Another factor, mentioned in the preceding principle, is the nature of the bonding of the oxygen in the anion, whether single or double. This factor may possibly be important in explaining pK differences among acids where the oxygen charge in the anion is nearly the same. For example, the charge on oxygen is about −0.44 in the anions of $H_3IO_6^=$, H_2O_2, $H_2PO_4^-$, $HSeO_4^-$, and

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[4] SANDERSON, R. T., "Chemical Periodicity," Reinhold Publishing Corp., New York, 1960.

HSO_4^-, whose pK values are 15, 11.7, 7.3, 2.1, and 2. It may be observed that the first two each possess two singly bonded oxygens per anion, and the third, one, while the last two have only doubly bonded oxygens. However, this concept appears to account for gross differences only and does not appear to be consistently useful for straightening out the correlation of Figure 1.

Other factors that would appear likely to influence the extent of acid dissociation of any hydrogen compound may be recognized from a consideration of the differences between two solutions, one containing the undissociated acid and the other its ions. Dissolution of these species must have a disruptive influence upon the dynamic structure of the water solvent that is different for the molecules than for the ions. In other words, the protonic bridging among water molecules may be broken down by one more than by the other. Furthermore, the interaction between water and acid molecules must certainly differ from that between water and the ions formed by dissociation. In addition, a not inconsiderable reorganization energy must be involved in the change from molecule to anion. Since all oxyacids must differ from one another with respect to these energy changes associated with dissolution and dissociation, it is not at all surprising that the condition of the combined oxygen as measured by partial charge can serve only as a very rough guide to understanding the relative strengths of oxygen acids.

The same principles that apply to oxides of different elements apply equally well to different oxides of the same element. As the competition among oxygen atoms for the valence electrons of a given atom increases, each oxygen becomes bonded less firmly by a less polar bond. This leads not only to reduced thermal stability, but also to weaker association productive of lower melting and boiling points and higher volatility. It causes the oxide to be less basic, more acidic, more of an oxidant. For example, MnO is a very stable solid having a standard heat of formation of −46 kcal per equivalent, melting at 1785°, weakly basic, and nonoxidizing. MnO_2 is too unstable a solid to be melted without decomposition, having a $\Delta H_f°$ of −31 kcal per equivalent, and is amphoteric and oxidizing. Mn_2O_7 is a liquid melting below 20°, very unstable, strongly oxidizing and strongly acidic. Although the exact partial charges on oxygen in these compounds are unknown, there is little reason to doubt that they become very substantially smaller from MnO to Mn_2O_7.

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Principles of Halogen Chemistry

The chemistry of the halogens covers a range far too wide to permit easy acquisition of a comprehensive yet well-organized picture. In an effort to pull together loose ends, to recognize unifying principles, and to help to compress the chief substance of this vast subject to something approaching the capacity of the average human brain, this paper has been written. It follows the general pattern of preceding articles in this series on chemical bonding (*1*), chemical reaction (*2*), and hydrogen chemistry (*3*).

The halogens, namely fluorine, chlorine, bromine, and iodine,[1] *are characterized by their similar electronic configurations which feature seven electrons in the outermost principal quantum level, and consequently the highest electronegativity in the respective period of each.* The high electronegativity arises from the fact that the mutual shielding by electrons filling the same principal quantum level is relatively small compared to the increased nuclear charge. This is in agreement with the relatively high compactness of the electronic clouds of atoms of these elements.

This outer shell similarity results in a reasonably close similarity of the halogens in their negative oxidation state of −1, because each atom, having one outermost half-filled orbital and a relatively high electronegativity, can form a single covalent bond in which it usually becomes the negatively charged partner. The general similarity of all the alkali halides well illustrates this point.

Significant dissimilarities among the halogens also occur, reflecting primarily the differences both in underlying and overlying atomic structures. The most important differences in underlying structure are in the penultimate shell, just below the outermost. In fluorine this contains only two electrons, in chlorine 8, in bromine and iodine, 18. In the overlying structures, stable *d* orbitals are unavailable in fluorine but available, and presumably increasingly so, in chlorine, bromine, and iodine. Since such orbitals appear to become stable mainly or only through partial removal of valence electrons and nothing can remove electrons from fluorine, the lack of *d* orbitals in fluorine has no practical importance except as an auxiliary explanation of the absence of positive oxidation states. But since both fluorine and oxygen are more electronegative than chlorine, bromine, and iodine, and chlorine more also than bromine and iodine, and bromine more than iodine (Table 1), there are numerous ways in which outer *d* orbitals can be made more available in these other halogens through oxidation. In positive oxidation states, the halogens can be expected to differ according to whether the penultimate shell is 8 (chlorine) or 18 (bromine and iodine).

The physical state of the halogens is determined by their existence as diatomic molecules and by the strength of van der Waals forces among these molecules. The diatomic molecules are the natural result of the limited bonding capacity of the halogen atoms, each of which can form but one single covalent bond. The van der Waals attractions among these diatomic molecules, being in general proportional to the population of the electron clouds and also inversely proportional to the tightness with which these electrons are held, are weakest in fluorine and increase as the halogens become larger. Table 1 gives the polarizabilities of the halogens and some of the physical properties which reflect the strength of the intermolecular forces. It will be observed that these properties all vary in the predictable direction.

Table 1. Some Properties of the Halogens

	F_2	Cl_2	Br_2	I_2
Atomic number	9	17	35	53
Electrons/molecule	18	34	70	106
Electronic configuration	2-7	2-8-7	2-8-18-7	2-8-18-18-7
Polarizability × 10^{24}, cc/mole	. . .	4.50	6.43	. . .
Bond length (Å)	1.44	1.99	2.28	2.66
Dissociation energy (kcal/mole)	38	57.2	45.4	35.6
Heat of atomization (kcal/mole)	38	57.2	53.4	51.0
First ionization energy of atom (kcal/mole)	402	300	273	241
Electronegativity	3.92	3.28	2.96	2.50
Melting point (°C)	−219.6	−102.4	−7.2	113.6
Heat of fusion (kcal/mole)	0.061	0.77	1.26	1.87
Boiling point (°C)	−187.9	−34.0	58.2	184.5
Heat of vaporization (kcal/mole)	0.78	2.44	3.59	4.99

The chemical reactivity of the halogens, to the extent that it depends on dissociation of the diatomic molecules, is generally high since the dissociation energies are relatively low, especially that of fluorine. The halogens as a group are quite reactive under relatively mild conditions. Fluorine is especially reactive, which may in part be a result of its low dissociation energy (see Table 1). This in turn has been explained as resulting from interference of nonbonding electron pairs on the adjacent atoms when they are bonded together. Such an interpretation is consistent with the well-known tendency of carbon, nitrogen, and oxygen to unite by multiple bonds, showing that when a single bond is formed between period 2 atoms, additional orbitals are brought close enough for interaction.

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[1] Little-known astatine is omitted from this paper because of its nuclear instability, scarcity, and present relative unimportance.

Bond energies of halides, per halogen atom, consistently show that the bond strength decreases in the order, fluoride ≫ chloride > bromide > iodide. Some typical examples are given in Table 2.

Table 2. Bond Energies of Some Typical Binary Halides (Heats of atomization per equivalent)

	Fluoride	Chloride	Bromide	Iodide
Li	202.4	164.7	148.8	128.7
Na	181.0	152.7	138.6	120.2
Mg	167.9	123.1	106.4	86.3
Ca	185.3	144.7	128.5	110.5
Al	163.7	109.8	94.5	76.4
C	102.6	79.9	...	...
Si	140.7	93.1	73.8	59.2
P(III)	...	82.2	69.1	55.7
As(III)	114.9	78.5	65.4	53.2

Bond energies of binary halides are in general directly proportional to the partial charge on halogen and the bond order, and inversely proportional to the bond length. An empirical equation representing this relationship is the following:

$$\delta_X = A\ nH/R + B$$

where δ_X is the partial charge on halogen, n is the bond order, H is the heat of atomization per equivalent, and A and B are constants characteristic of the halogen. This relationship holds for practically all solid binary halides and approximately for most liquid or gaseous molecular halides as well (*4*).

Whenever the simplest possible binary halide molecule would possess unoccupied low energy orbitals, in addition to the unshared electron pairs always present on the halogen atom, the molecules condense to a more highly associated state under ordinary conditions, and possess the physical properties predictable for such a state. This condensation is to what is called the ionic state when the bond polarity is high and to what might be called coordination polymers when the polarity is less. These are probably different degrees of the same phenomenon, which is a general tendency for molecules to make maximum possible use of all available outer orbital vacancies (*1*). The coordination number of the halogen atom in these condensed states is at least partly dependent on the amount of partial negative charge it bears. Even in the most ionic crystals, bonding may usefully be regarded as essentially donor-acceptor interaction, with all outermost electrons acting as valence electrons and all partially positive atoms furnishing all available vacant outer orbitals as acceptors (*4*). The coordination number of the halogen depends chiefly on its partial charge but also on its original electronegativity. The donating power is greater the higher the negative charge but lower, the more electronegative the donor atom was initially. For this reason, for a given amount of charge, halogen coordination number tends to increase in the order F-Cl-Br-I.

Properties such as melting point, heat of fusion, boiling point, and heat of vaporization reflect the magnitude of the forces of aggregation, and thus tend to be higher for more polar compounds in closely coordinated lattices, and also higher in the sequence, iodides, bromides, chlorides, and fluorides. Some illustrative examples are given in Table 3.

The only known exceptions to this principle are the boron halides, which presumably have one vacant orbital if the three halogen atoms are attached to the boron by single covalent bonds, and yet are molecular, being monomeric in the gas phase. In these it is possible that the otherwise vacant orbital on boron becomes involved in partial double bond formation, using otherwise unshared electron pairs on the three halogen atoms. In part at least, this hypothesis is supported by the shorter than expected bond length in BF_3 and by the order of Lewis acid strength increasing from BF_3 to BBr_3 (*5*), in keeping with the diminishing ability of the larger halogen to become multiple bonded to the boron. The aluminum halides appear to use the fourth aluminum orbital on the monomer to form dimeric molecules by halogen bridging (except for aluminum fluoride which condenses more highly), and all other halides condense even further if orbital vacancies would otherwise be left free.

Halides in which the halogen has acquired relatively large negative charge tend to be high melting and low in volatility. This is very similar to the preceding principle because the kind of element from which halogen can acquire relatively high negative charge is that which is low in electronegativity and thus also a metal having more outermost vacancies than valence electrons, per atom. Binary halides that contain highly polar bonds therefore invariably would have also vacant low energy orbitals in the simplest possible molecules. Condensation to make fuller use of these orbitals therefore occurs.

Table 3. Properties of Some Halides with Relatively High Charge on Halogen

	Charge on halogen	mp (°C)	$\Delta H°_{fusion}$ (kcal/mole)	bp (°C)	$\Delta H°_{vap}$ (kcal/mole)	$\Delta H°_f$ (kcal/equiv)
NaF	−0.75	995	7.8	1704	50	−136.0
NaCl	−0.67	808	6.8	1465	40.8	−98.2
NaBr	−0.62	755	...	1390	...	−86.0
NaI	−0.54	661	...	1300	...	−68.8
MgF_2	−0.34	1263	13.9	2227	65	−131.8
$MgCl_2$	−0.28	714	10.3	1418	32.7	−76.7
$MgBr_2$	−0.25	711	...	...	...	−61.9
CaF_2	−0.47	1418	7.1	2500	...	−145.2
$CaCl_2$	−0.40	782(P)	6.8	...	...	−95.0
$CaBr_2$	−0.36	760	...	810	...	−80.7
CaI_2	−0.30	740	...	714	...	−63.9
ZnF_2	−0.24	872	...	1502	...	−48.2(?)
$ZnCl_2$	−0.18	275	5.5	756	15.5	−49.7
$ZnBr_2$	−0.15	394	...	650	...	−39.1
MnF_2	(−0.30)	856	...	...	...	−95
$MnCl_2$	(−0.25)	650	...	1190	...	−57.7

Table 4. Properties of Some Halides with Relatively Low Charge on Halogen

	Charge on halogen	mp (°C)	ΔH°_{fusion} (kcal/mole)	bp (°C)	ΔH°_{vap} (kcal/mole)	ΔH°_f (kcal/equiv)
SF_6	−0.05	−50.7(P)	1.20	−63.7(*s*)	5.46(*s*)	−44
AsF_3	−0.11	−5.95	2.5	58	...	−72.8
IF_7	−0.06	4.5	...	5.5	7.37	...
GeF_4	−0.16	−15.0(P)	...	−36.8(*s*)	7.8(*s*)	...
NF_3	−0.07	−208.5	...	−129.1	2.93	−9.1
WF_6		2.3	2.5	17.1	6.2	...
CCl_4	−0.06	−22.9	0.60	76.7	7.17	−8.3
PCl_3	−0.10	−92	...	76	7.28	−27.0
$TeCl_4$	−0.06	224.1	...	388	...	−19.3
ICl	−0.13	27.3	1.83	...	...	4.2
$BiCl_3$	−0.11	232	2.6	441	...	−30.2
S_2Cl_2	−0.09	−80	...	138	...	−7.2
$TaCl_5$	...	217	...	233	13.1	...
WCl_6	...	275	...	347	...	...
BBr_3	−0.11	−46	...	90.5	...	−17.6
$SiBr_4$	−0.11	5.2	...	152.8	...	−23.8
$SbBr_3$	−0.07	96.6	...	280	...	−20.7
$TeBr_2$	−0.07	25	...	...	...	...
AsI_3	0	146	...	(400)	...	−4.6
TeI_4	−0.01	150	...	365	...	−25.5
SiI_4	−0.07	120.5	...	290	...	−7.9

This effect is usually indistinguishable from a so-called cation-anion attraction, or an attractive electrostatic interaction among polar bonds. The physical properties (Table 3) are those predictable for such highly condensed aggregates.

Whenever the simplest possible binary halide molecule contains no available low energy orbital vacancy, no further condensation of the compound is possible except through relatively weak van der Waals interactions. Consequently the physical properties of such compounds can be predicted to be consistent with the molecular state. All such compounds are molecular, and if solid, are relatively low melting, and volatile, involving only relatively small enthalpy changes in the usual changes of phase. Many are liquid or gaseous at ordinary temperatures. Bonds in such compounds are of generally low polarity, which itself would limit the force of intermolecular attractions. But both low polarity and lack of unoccupied orbitals occur together, since elements whose atoms have as many or more outermost electrons as vacancies and therefore can leave no vacancies after covalent bonding are also elements which are relatively high in electronegativity and therefore cannot form very polar bonds with the halogens. Some typical molecular halides are listed with some of their properties in Table 4.

Halides in which the halogen has not acquired much negative charge tend to be low melting and volatile. In effect, this is nearly equivalent to the preceding principle. Compounds of halogens with elements that do not give up electrons easily have weak intermolecular attractions for two reasons. One is the low polarity of bonds between elements both of which are relatively high in electronegativity, affording little dipole-dipole interaction. The other is the absence of outer orbital vacancies on atoms of the more electronegative elements once they have formed their quota of conventional covalent bonds, thus eliminating the possibility of condensation through donor-acceptor interaction.

Compounds of halogens with elements that do give up electrons easily may also have low negative charge per halogen atom if several halogen atoms are competing for the electrons of the same other atom. The electronegativity of the central atom is increased to the extent that electrons are withdrawn from it, so that when several halogen atoms are pulling on its electrons, the central atom relinquishes only a little to each. Not only is each bond therefore less polar, but also the central atom commonly is so well surrounded by the halogen atoms that the exterior of the molecule is essentially all halogen and there is no opportunity for strong intermolecular attractions. Some examples of halides of low charge on halogen and their physical properties are given in Table 4.

The oxidizing (or halogenating) power of halides is inversely proportional to the partial negative charge on halogen. An atom of halogen does not lose its potential electron-attracting power merely by forming a covalent bond. It must succeed, through forming this bond, in acquiring substantial partial negative charge to become reduced in electronegativity. Otherwise it remains, in the compound, a potential halogenating agent from which the halogen may break loose if more favorable control of electrons becomes available to it from some other atom. All compounds in which the partial negative charge on halogen is not very high are therefore potential halogenating agents. These include not only halides of elements initially high in electronegativity but also polyhalides of elements initially low in electronegativity, in which the competition among halogen atoms prevents acquisition of substantial negative charge by any one of them. The compounds of Table 4 are all examples of potential halogenating agents. The ease of reaction will of course vary widely, depending on the available mechanisms by which the reaction might occur. We would not think, for example, of CCl_4 or SF_6 as active halogenating agents at ordinary temperatures, not because they cannot give up halogen or because the halogen in them is already highly negative, but because the means of doing so is limited by their structures which protect the bond to halogen from outside influence under these conditions. Mixing such compounds with strong reducing agents in a reactive form is therefore certain to be potentially hazardous since once it starts, reaction may be expected to be highly exothermic and probably autocatalytic.

On the other hand, halides having highly negative halogen cannot be very active oxidizing agents because their halogen has lost most of its electronegativity by combining. Sodium chloride, for example, is in no ordinary sense an oxidizing agent. But as the negative charge becomes less, a halide gains in oxidizing power, and becomes capable of oxidizing strong, and then weaker, reducing agents.

The reducing power of halides is directly proportional to the partial negative charge on halogen, and for the same partial charge increases in the order F-Cl-Br-I. The halide negative ions have the highest reducing power possible for halogen, but since the initial electronegativity of all halogens is relatively high, they cannot be expected to give up electrons very easily once they have acquired them. Iodide ion is the best reducing agent of the group in keeping with its lowest initial electronegativity. Fluoride ion cannot be reduced except by a positively charged electrode because no chemical agent can remove the extra electron in competition with fluorine. The electrode oxidation potentials for the reactions $2\ X^- = X_2 + 2e^-$ are: fluorine -2.87, chlorine -1.36, bromine -1.07, and iodine -0.54 v.

The greater bond energy of the smaller and more electronegative oxygen combined with other elements makes their bromides and iodides especially susceptible to atmospheric oxidation. As might be expected, the halogens may also be displaced from their halides by more electronegative halogens.

Although halogen atoms themselves cannot ordinarily function as electron acceptors, their compounds can if the simplest molecules would contain outer shell low energy vacant orbitals. This property is, however, primarily that of the element other than halogen, although the property is enhanced by electron withdrawal from the central atom by the halogen atoms. It results in the formation of many complexes, including complex halides where the donor is more negative halogen from another compound, such as the halide ion forming BF_4^- or PF_6^-. Some of the best known Lewis acids are boron and aluminum halides; any other metallic halide might so function, to the extent that the metal atom can act as acceptor. As mentioned earlier, such reaction among like molecules can lead to association such as dimerization of $AlCl_3$ or polymerization of $ZnCl_2$. Between unlike molecules the reaction can produce a large number of molecular addition compounds such as $BF_3 \cdot O(CH_3)_2$.

The complexing ability of halides as donors is proportional to the partial negative charge on halogen. The charge on fluorine (-0.25) in HF, for example, is insufficient to permit the fluorine to form stable complexes as donor. Acids such as HBF_4 or HPF_6 are only hypothetical and exist only as the ionized form in solution, where the negative fluoride ion is the donor. Similarly, complex chlorides are not formed by HCl in which the charge on chlorine is -0.16 although more negative chlorine, especially chloride ion, readily forms them. As already mentioned, such complexing results in condensation of metal halides to ionic or polymeric crystalline forms, in many of which halogen bridges hold the metal atoms together.

Only hydrogen fluoride of all the hydrogen halides is associated at ordinary temperatures by protonic bridging, because fluorine alone of the halogens offers its outer electron pairs in sufficient spatial concentration to attract a partially positive hydrogen or a proton. The requirements for protonic bridging are attached hydrogen bearing partial positive charge, and a small negatively charged atom having unshared outer electron pairs available. All the hydrogen halides satisfy the first requirement (although hydrogen iodide would satisfy it least). The second requirement is not met by larger atoms because, apparently, an electron pair spreads out to the greatest possible extent and thus becomes less available to a protonic hydrogen of another molecule. In fluorine the smaller area available per electron pair restricts the negative charge to a region where more effective interaction with a positive hydrogen can occur.

The availability of an electron pair on fluoride ion is greater than on the fluorine in HF, so if protonic bridging can occur in HF it certainly ought to occur between HF and a fluoride ion. If it should, however, there would be, in effect, two fluorine atoms competing for the same hydride ion or two fluoride ions competing for the same proton (*6*). Neither of these hypothetical possibilities could result in an unsymmetrical bonding arrangement, because to the hydrogen the two fluorines must be exactly equivalent. A symmetrical bifluoride ion therefore results: $(F{-}H{-}F)^-$. Hydrogen here is clearly divalent, which apparent violation of the Pauli exclusion principle may be rationalized by pointing out that the average occupancy of the hydrogen orbital does not exceed two electrons, but is only 1.04. This interpretation obviously distinguishes the bifluoride ion from examples of ordinary protonic bridging, a distinction borne out by the much higher bond energy (25–30 kcal instead of 5–10) in the bifluoride ion and the even spacing of the hydrogen halfway between the fluorines. Evidence of similar bihalide ions of the other halogens has recently been reported (*7*).

The hydrogen halides increase in acid strength from hydrogen fluoride to hydrogen iodide. The same factors that contribute to protonic bridging appear to influence the action of a halide ion as electron donor to a bare proton. If the electron pair on the halide ion is concentrated within a small enough area, as in fluoride, the proton can be effectively coordinated to it. Otherwise, the coordination is weaker. The acid strength of a hydrogen compound in a solvent is a function of the competition between solvent molecules and hydrogen compound anion for the proton. The greater the relative donor ability of the solvent, the greater the acidity. In a solvent such as water, only fluoride of the halide ions is an effective competitor at ordinary dilutions, with the result that hydrogen fluoride is a weak acid but the other hydrogen halides are strong acids. In water these others become leveled to the strength of hydronium ion, but in more acidic solvents the strength (as proton donor) is shown to increase in the order $HF < HCl < HBr < HI$.

The halogens differ from one another most notably in their positive oxidation states. The electronic basis for these differences was partly explained under the third principle. In addition, the differing electronegativities affect the properties of compounds in these states. Such states are produced chiefly by fluorine and oxygen, whose high electronegativity gives them power to promote electrons from the *p* orbitals of chlorine, bromine, and iodine to the outer *d* levels. Each such promotion of one electron produces a new half-filled orbital and leaves behind a half-filled orbital, simultaneously creating the requisites for forming two new covalent bonds. The oxidation states thus observable are therefore −1, 0, 1, 3, 5, and 7. Formal oxidation states having other values (e.g., 4 and 6) are also observed but only where multiplicity in the bonding makes uncertain the actual number of electrons involved.

Before attempting to explain differences among chlorine, bromine, and iodine in these states we must consider what these differences are. In the +1 state, we find all three forming fluorides XF, presumably. That is, ClF is most stable, but BrF, and IF if it is formed at all, appear rapidly to disproportionate forming bromine or iodine and higher fluorides. Similarly, Cl_2O, although not very stable, is most stable of the three, Br_2O is stable only below −40°C, and I_2O has not been isolated. None of the hypohalous acids has been isolated because of their instability. The very weak hypochlorous acid and its salts slowly lose oxygen from solution, the salts less rapidly. Disproportionation occurs readily, forming chloride and chlorate. Hypobromous acid and salts differ in being much less stable and much more readily disproportionating to bromide and bromate, and the acid is much weaker. Hypoiodous acid is weaker still, somewhat more basic than acidic, and even less stable toward decomposition and disproportionation than HOBr. Fluorine forms ClF_3 and BrF_3, but IF_3 appears to be unknown.

No halogen oxides having halogen in the +3 state are known, but one very unstable acid, HOClO, representing this state exists in solution and as unstable salts. Similar compounds of bromine and iodine are unknown.

Chlorine does not form fluorides higher than ClF_3, but bromine and iodine both form pentafluorides. These are both very stable, BrF_5 a little more than IF_5, but quite reactive as fluorinating agents. Neither chlorine nor bromine form (V) oxides but iodine forms the stable I_2O_5, which appears to be a polymeric solid. Although both chlorine and bromine form halic acids in aqueous solution, too unstable to be isolated, of formula $HOXO_2$, iodine forms the stable $HOIO_2$ which loses water when heated mildly to form HI_3O_8 that can be dehydrated completely to I_2O_5 by heating above 195° C. Iodic acid tends to polymerize in solution; it is fairly strong but weaker than either chloric or bromic acids.

The only halogen heptafluoride is that of iodine, a gaseous compound that as expected is an active fluorinating agent. Chlorine forms the (VII) oxide, Cl_2O_7, but no such compound of bromine or iodine is known. Perchloric acid, $HOClO_3$, a very strong acid, is the most stable of the oxychlorine acids and its salts are likewise the most stable salts. Yet no similar compounds of bromine are known. Iodine forms a solid periodic acid of formula H_5IO_6, a weak pentaprotic acid forming fairly stable salts. Such salts also form in the decomposition of iodates.

Finally, the following other compounds exist, having no congeners among the other halogens: Cl_2O_6, ClO_3, Br_3O_8, I_4O_9, OF_2, O_2F_2, and possibly a few more.

To find by examination of all these data some simple and consistent explanation of these differences is perhaps more than should be expected. It may be useful to note, however, that the halogens are not unique in their high degree of individuality within the same periodic group. Quite similar differences are to be noted among sulfur, selenium, and tellurium, and likewise among phosphorus, arsenic, and antimony, or even farther to the left in the periodic table. For example, Cl_2O_7 is volatile and although unstable, is not difficult to prepare, analogous oxides of bromine are unknown, but iodine, although it does not form a (VII) oxide, forms a stable polymeric I_2O_5. SO_3 although tending toward polymerization is volatile and easily prepared, SeO_3 is more polymeric, difficult to prepare, and decomposes above 180°, but the highly polymeric TeO_3 is stable to 700° C. For the hexafluorides, the heats of atomization are SF_6 72, SeF_6 68, and TeF_6 79 kcal per equivalent. In Group V-A, phosphorus is more stable in its (V) state than either arsenic or antimony, but antimony (V) seems somewhat more stable than arsenic (V), as evidenced by the greater thermal stability of the oxide and the existence of only the antimony chloride. Heats of atomization of the (III) halides are PCl_3 82.2, $AsCl_3$ 78.5, and $SbCl_3$ 79.9; PBr_3 69.1, $AsBr_3$ 65.4, and $SbBr_3$ 68.3; and PI_3 55.7, AsI_3 53.2, and SbI_3 54.1 kcal per equivalent. In Group IV-A, GeO_2 melts lower (1116°) than either SiO_2 (1710°) or SnO_2 (1927°C) and has a lower heat of formation per equivalent (−32.1) than SiO_2 (−51.3) or SnO_2 (−34.7).

There is thus indicated a hazy but moderately consistent picture of period 4 elements differing from both upper and lower neighbors in their respective major groups, especially to the right in the periodic table. The electronic difference from the neighbor above is that brought about by the interposition of the first transition series: from a penultimate shell of 8 to one of 18. The neighbor below, on the other hand, is electronically similar, having also a penultimate shell of 18. The changes that accompany the change from 8 to 18 in the penultimate shell include greater compactness (and therefore relatively smaller atoms than otherwise expected), higher electronegativity (although the difference diminishes as the outermost shell becomes filled), and correspondingly less polar and weaker bonds to more electronegative elements. On this basis it is relatively easy to rationalize the differences between silicon and germanium, phosphorus and arsenic, sulfur and selenium, or chlorine and bromine.

A somewhat greater difficulty is presented by the need to explain the differences between 18-shell elements of period 4 and 18-shell elements of period 5. One fundamental cause of such differences is a decrease in electronegativity with higher atomic number within the group. This decrease is probably caused chiefly by the increase in size, requiring the approximately equally effective nuclear charge to operate over a greater distance. In fact, the product of covalent radius and electronegativity is practically constant for each of the pairs of elements, Ge-Sn, As-Sb, Se-Te, and Br-I. This increase in radius not only decreases the electronegativity but also makes the outer *d* orbitals more readily available for bonding. "Expansion of the valence octet" may therefore occur more easily, the bonds thus formed having greater stability both because of greater orbital availability and greater bond polarity. In particular, high positive oxidation states are more stable in iodine than in bromine, in tellurium than in selenium, and in antimony than in arsenic. The electronegativities of these pairs are I 2.50 and Br 2.96, Te 2.34 and Se 2.76, and Sb 2.19 and As 2.53.

One may note also a tendency toward diminishing bond multiplicity with increasing size of atom. Oxygen-chlorine bonds tend to be double bonds but iodine-oxygen compounds tend to be polymeric with each oxygen forming two single bonds. The tendency to form ortho acids, with single bonds to hydroxyl in place of double bonds to oxygen, is consistent also. But single bonds tend to become more stable with increased polarity. We may look upon bromine-oxygen bonds as involving too great a difference in atomic radii to permit stability through multiplicity yet having too little polarity for stability as single bonds. In contrast, chlorine-oxygen bonds although even less polar can be stable through multiplicity involving the smaller chlorine atoms. Iodine-oxygen bonds although not stably multiple are stable owing to their higher polarity arising from the much lower electronegativity of iodine. In this view, bromine is left relatively impotent with respect to combining with oxygen, forming only bromates having appreciable stability. Multiple bonds of oxygen to other atoms appear generally to be stabilized by the acquisition of extra electrons to form polyatomic anions (*8*), and the bromates are no exception.

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La chimie des molécules "sandwich"

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Il y a très exactement un siècle (c'était en mars 1863), Wurtz professait devant la Société Chimique de France une série de leçons qui s'intitulait « Alliance de la Chimie Organique et de la Chimie Minérale ».

Dans l'esprit de Wurtz il s'agissait essentiellement de démontrer que les lois qui régissaient ces deux domaines de la chimie étaient analogues. Les travaux de Werner sur les complexes devaient quelques années plus tard étendre ces conceptions au domaine de la stéréochimie.

Les complexes de Werner célébraient en effet cette alliance à plusieurs points de vue : ils montraient que la possibilité de substitution progressive était applicable aux complexes, que des radicaux organiques pouvaient être partie intégrante d'un agrégat moléculaire contenant un métal, enfin, que la structure des complexes, comme celle des dérivés du carbone, relevait du domaine de la stéréochimie.

Au début du siècle, la découverte des réactifs de Grignard devait montrer l'intérêt synthétique considérable des organométalliques en Chimie Organique.

Pourtant, jusqu'à la découverte des molécules « *sandwich* », les chimistes n'espéraient guère pouvoir introduire dans un squelette moléculaire des liaisons *métal-carbone* suffisamment stables pour autoriser à opérer sur ce squelette les multiples transformations qui caractérisent la chimie organique.

Cette possibilité existe depuis la découverte des molécules « sandwich ».

La découverte des molécules « sandwich » est d'ailleurs purement forfuite.

En 1951, deux professeurs de Glasgow, Kealy et Pauson, cherchaient à isoler le bicyclopentadiényl, C_5H_5-C_5H_5, par action du magnésien du cyclopentadiène sur le chlorure ferrique.

Et, au lieu d'obtenir le composé attendu, ils isolèrent un composé orange extrêmement stable qui répondait à la formule $C_{10}H_{10}Fe$. Cette formule fait évidemment penser à un organo-métallique. Mais le composé isolé ne présentait aucune des propriétés classiques des organo-métalliques.

Tout d'abord, il est extrêmement stable. Il fond à 173° et peut être chauffé sans décomposition jusqu'à 470°. Il peut être entraîné à la vapeur d'eau sans décomposition. Il résiste à l'action des bases et des acides dilués.

D'autre part, il possède des propriétés aromatiques et se prête par exemple très bien à des réactions de Friedel et Crafts,

Enfin, le squelette global de la molécule peut être soumis à de nombreuses réactions chimiques sans altération et surtout sans rupture des liaisons fer-carbone.

Ces premières considérations et l'analyse critique de plusieurs données physico-chimiques amenèrent à proposer pour ce composé une structure « sandwich ».

Dans cette structure l'atome de fer se trouve pris en « sandwich » entre les deux anneaux cyclopentadiéniques. Le composé $C_{10}H_{10}Fe$ a été appelé ferrocène. Cette terminologie se propose de rappeler que le ferrocène possède des propriétés assez voisines de celles du benzène.

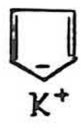
La découverte du ferrocène a été le point de départ de toute une chimie nouvelle des dérivés du cyclopentadiène.

A l'heure actuelle, les dérivés du cyclopentadiène se classent en 3 groupes principaux :

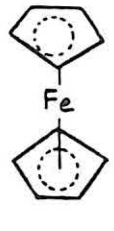
a) Tout d'abord, les composés ioniques dont le type même est le dérivé potassé qui, lui, se comporte comme un organo-métallique classique (I).

b) Ensuite les dérivés du type ferrocène ou « sandwich » symétrique (II).

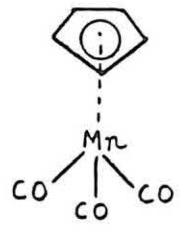
c) Puis des dérivés qu'on peut appeler des « sandwichs » dissymétriques. Le type même de ces composés est le cyclopentadiényl-manganèso tricarbonyle (ou cymantrène). Dans ce type, l'atome métallique est pris en sandwich entre un anneau cyclopentadiénique et trois groupements CO (III).



(I)



(II)



(III)

PREPARATION DES CYCLOPENTADIENYLES SYMETRIQUES ET DES DERIVES DU FERROCENE

Les « sandwichs » symétriques s'obtiennent facilement par action d'un dérivé ionique du cyclopentadiène sur un dérivé métallique.

L'apport métallique peut se faire sous forme d'halogénure, de thiocyanate, d'acétonylacétate, de métal carbonyle ou, dans quelques cas, du métal lui-même :

$$2\ C_5H_5MgBr + FeCl_2 \rightarrow (C_5H_5)_2Fe + MgCl_2 + MgBr_2$$

$$2\ C_5H_5Na + MX_n \rightarrow (C_5H_5)_2MX_{n-2} + 2\ NaX$$

$$\left\{\begin{aligned} &2\ C_5H_5Na + Ni(NH_3)_6(SCN)_2 \rightarrow Ni(NH_3)_6^{++}(C_5H_5^-)_2 \ldots \\ &\qquad\qquad\qquad\qquad \ldots + 2\ NaSCN \\ &Ni(NH_3)_6^{++}(C_5H_5^-)_2 \rightarrow 6\ NH_3 + (C_5H_5)_2Ni \end{aligned}\right.$$

$$Cr(CO)_6 + 2\ C_5H_6 \rightarrow Cr(C_5H_5)_2 + 6\ CO + H_2$$

En utilisant ces différents procédés on a pu synthétiser toute une série de cyclopentadiényles. La variante peut porter soit sur le métal, soit également sur la nature des deux anneaux du sanwich.

Le tableau ci-dessous indique les principaux métaux qui ont pu être introduits dans un sandwich. Ces métaux appartiennent aux groupes IV à VIII. La troisième colonne du tableau schématise le métallocène (π est le sigle de la liaison et C_p désigne le reste C_5H_5). La quatrième colonne donne la formule de composés apparentés correspondant à un degré d'oxydation différent.

PRINCIPAUX di π-CYCLOPENTADIENYLES

Groupe IV	Ti	π — Cp_2 Ti	π — Cp_2 T X_2
	Zr	»	π — Cp_2 Zr X_2
V	V	π — Cp_2 V	π — Cp_2 V.X_2
	Nb	»	π — Cp_2 Nb Br_3
	Ta	»	π — Cp_2 Ta Br_3
VI	Cr	π — Cp_2 Cr	
	Mo	»	π — Cp_2 Mo H_2
	W	»	π — Cp_2 W H_2
VII	Re	π — Cp_2 Re H	
VIII	Fe	π — Cp_2 Fe	π — Cp_2 Fe^+
	Ru	π — Cp_2 Ru	π — Cp_2 Ru^+
	Os	π — Cp_2 Os	»
	Co	π — Cp_2 Co	π — Cp_2 Co^+
	Rh	»	π — Cp_2 Rh^+
	Ir	»	π — Cp_2 Ir^+
	Ni	π — Cp_2 Ni	π — Cp_2 Ni
	Pd	π — Cp_2 Pd	»

La variante peut également porter sur la partie organique de la molécule.

On connait des dérivés de l'*indène,* des dérivés *aromatiques* dont le type est le dibenzène chrome, des dérivés du *cycloheptatriène,* de l'azulène et également du butadiène et du thiophène.

PROPRIETES PHYSIQUES DU FERROCENE

Il existe actuellement plusieurs centaines de squelettes « sandwich » différents. Mais, parmi tous ceux-ci, seul le ferrocène (et à un degré moindre le cyclopentadiényl-manganèse-tricarbonyle) a été le support d'une chimie organique entièrement originale. Nous nous limiterons à cet aspect particulier de la chimie des molécules « sandwich ».

La chimie du ferrocène est, pour une grande partie, une conséquence de sa structure « sandwich ».

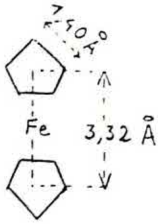
Cette structure a pu être établie par un ensemble de données physico-chimiques.

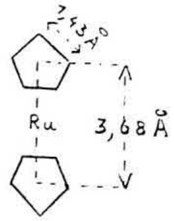
Le spectre infrarouge tout d'abord montre qu'il n'existe qu'une seule vibration CH. Ceci implique évidemment l'équivalence des dix hydrogènes.

Le moment dipolaire du ferrocène est nul et les moments dipolaires des dérivés mono et diacétylés sont compatibles avec la *libre rotation* autour de l'axe de la molécule.

Mais c'est surtout *l'analyse aux rayons X* qui a permis d'établir la structure du ferrocène.

Cette analyse a été faite par deux chercheurs allemands (Dunitz et Orgel) et ces auteurs ont proposé le terme de « Doppelkegelstruktur » pour ce type de molécules. Il est d'ailleurs curieux de noter que le ferrocène a la structure antiprisme alors que le ruthénocène a la forme éclipsée.





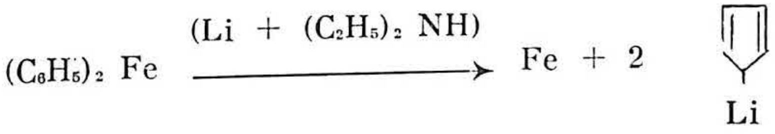
On a attribué cette propriété à la différence d'encombrement entre le fer et le ruthénium. Si l'atome central est petit (cas du fer), la répulsion qui s'exerce entre les atomes d'hydrogène impose la conformation décalée.

Quant à la structure électronique, elle semble moins bien établie. L'interprétation la plus simple revient à considérer que l'atome de fer acquiert la configuration d'un gaz rare (le krypton) par passage des 12 électrons π des deux noyaux sur les orbitales libres 3 *d*, 4 *s* et 4 *p*. Cette interprétation simpliste se prête à de sérieuses critiques. En particulier, elle conduit à envisager un déficit électronique sur les noyaux cyclopentadiéniques. Ce déficit est incompatible avec *les propriétés aromatiques* qui supposent une forte disponibilité électronique.

Seule la théorie des orbitales moléculaires semble conduire à une interprétation correcte.

— *Stabilité de la molécule.*

L'expérience indique que cette structure confère à la molécule une grande stabilité. Nous avons déjà noté que le ferrocène peut être chauffé sans décomposition jusqu'à 470°. Il fond à 173° et peut être entraîné à la vapeur d'eau. Il résiste à l'action des acides et des bases dilués et est stable à l'eau jusqu'à 350°. La liaison Fe-carbone peut toutefois être rompue par le lithium dans l'ammoniac ou l'éthylamine



Le ferrocène résiste à l'hydrogénation en présence des catalyseurs usuels et le caractère diénique du cyclopentadiène est totalement masqué. Par contre, il présente des propriétés chimiques typiques.

PROPRIETES CHIMIQUES DU FERROCENE

Ces propriétés chimiques sont une conséquence directe de sa structure. On peut les classer autour de trois groupes principaux.

1. — La présence des deux nuages d'électrons π des restes *cyclopentadiéniques* confère au ferrocène des propriétés *aromatiques*.

2. — La structure « sandwich » correspond à une géométrie particulière qui se manifeste essentiellement par des *phénomènes d'isoméries nouveaux*.

3. — Enfin, la présence de l'atome de *fer* implique diverses conséquences physico-chimiques : *liaisons H intramoléculaires, protonation facile du squelette, stabilité des ions α - ferrocényl carbonium*, enfin, *existence du système oxydo-réducteur :*

ferrocène — e ⇄ ion ferricinium

Les propriétés aromatiques du ferrocène

Le caractère aromatique du ferrocène a été reconnu dès sa découverte. Woodward réussit en effet en 1952 à préparer le diacétylferrocène par réaction de Friedel et Crafts. Toutefois, si l'on veut établir un parallélisme entre le ferrocène et le benzène, il est indispensable d'avoir toujours présent à l'esprit l'oxydation possible du ferrocène. Ce parallélisme peut s'établir en cinq points :

a) En principe toutes les réactions du benzène qui ne mettent pas en jeu des réactifs oxydants sont transposables dans la série du ferrocène.

b) Le ferrocène présente un caractère acidique et nucléophile un peu plus accentué que le benzène.

c) Mais les attaques électrophiles oxydantes s'accompagnent toujours d'une oxydation en ion ferricinium. Cet ion devient alors insensible à l'agent électrophile.

d) Il en résulte que certaines préparations classiques de la série benzénique ne peuvent s'appliquer à la série du ferrocène. Il faut alors utiliser des procédés détournés et des méthodes parfois inattendues.

e) Enfin les dérivés du ferrocène présentent qualitativement les mêmes propriétés que ceux du benzène. Mais le caractère nucléophile du ferrocène influe quantitativement sur ces propriétés. Cette originalité apparaît si on passe en revue les différentes fonctions qui ont pu être greffées sur le squelette.

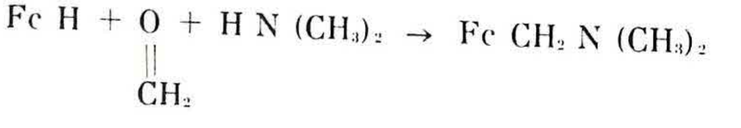
-- *Métalation et mobilité de l'hydrogène.*

Il apparaît tout d'abord que l'H du ferrocène est plus mobile que celui du benzène.

Le dérivé lithien se prépare facilement par réaction d'échange avec le butyl-lithium. On obtient d'ailleurs un mélange de mono et de dilithien 1—1' (hétéroannulaire). D'autre part le ferrocène se mercurise plus facilement que le benzène par l'acétate mercurique. Les dérivés lithiens et mercuriques seront des points de départ importants pour la synthèse des autres composés.

La mobilité de l'hydrogène apparaît également dans la réaction d'aminoalcoylation.

Le ferrocène se prête en effet à la réaction de Mannich comme le phénol.



$$\mathrm{Fc\,H} + \underset{\underset{\displaystyle \mathrm{CH_2}}{\|}}{\mathrm{O}} + \mathrm{H\,N\,(CH_3)_2} \rightarrow \mathrm{Fc\,CH_2\,N\,(CH_3)_2} \quad (*)$$

-- *Halogénation, nitration, sulfonation.*

Il n'est pas possible de comparer directement le ferrocène et le benzène vis-à-vis des réactifs électrophiles classiques car l'action de ces réactifs (NO_2^+, SO_3H^+, Cl^+)

(*) Le radical C_5H_5 Fe C_5H_4 est généralement désigné par Fc. Avec cette convention, le ferrocène sera représenté par FcH.

s'accompagne toujours d'une oxydation ou d'une rupture des liaisons carbone-fer.

Les dérivés *halogénés* du ferrocène ne sont donc pas accessibles par voie directe mais on peut les préparer par action des halogènes sur les dérivés mercuriques. Avec l'iode on obtient d'ailleurs des composés poliiodés intermédiaires.

$$\mathrm{Fc\ Hg\ Cl} \xrightarrow{2\ I_2} \mathrm{Fc\ Hg\ Cl,\ 2\ I_2} \xrightarrow{I_2} \mathrm{Fc\ I,\ 2\ I_2} \xrightarrow{Na_2S_2O_3} \mathrm{Fc\ I}$$

La *sulfonation* directe du ferrocène est également impossible mais on a pu toutefois obtenir le dérivé mono et le dérivé disulfoné par action des mélanges : pyridine + SO_3, dioxanne + SO_3, ou plus simplement en employant l'anhydride acétique comme solvant.

La *nitration* doit également faire appel à des procédés indirects. Il a fallu attendre 1959 pour trouver mention dans la littérature du nitroferrocène. Deux auteurs ont alors signalé sa préparation à partir de FcLi à — 70°.

— *Formylation et acylation.*

Par contre la *formylation* et *l'acylation* du ferrocène ne présentent aucune difficulté.

Le ferrocènealdéhyde s'obtient très facilement par action du N-méthylformanilide et de la diméthylformamide.

L'acylation selon *Friedel et Crafts* est certainement la réaction la plus souvent utilisée.

Cette acylation peut se faire soit avec les chlorures d'acides soit avec les anhydrides d'acide.

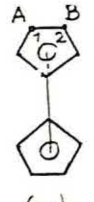
Il est curieux de noter que des quantités équimoléculaires de FcH, CH_3COCl et $AlCl_3$ donnent uniquement le dérivé monoacétylé. Mais en présence d'un excès de $AlCl_3$ on obtient presqu'exclusivement le dérivé diacétylé hétéroannulaire.

L'ASPECT TRIDIMENSIONNEL

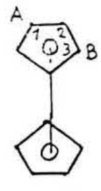
L'aromaticité du ferrocène se superpose à des propriétés géométriques caractéristiques de la structure « sandwich ». Et on a parlé à ce sujet d' « aromaticité à trois dimensions ». Les conséquences de ce caractère tridimensionnel sont multiples.

— *Isomérie homo et hétéroannulaire.*

Considérons tout d'abord un dérivé disubstitué. Si la molécule était rigide on devrait prévoir l'existence de *cinq isomères*. S'il y a libre rotation on n'en trouvera que *trois*. (IV à VI).



(IV)



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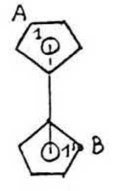
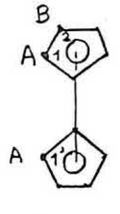
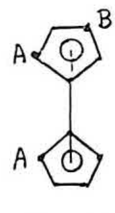


(VI)

HOMO HETERO



(VII)



(VIII)

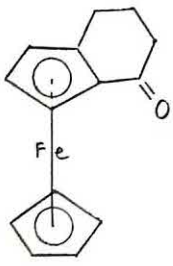
On a effectivement isolé trois diacétylferrocènes, trois méthylacétylferrocènes. Mais on n'a jamais réussi à en isoler plus de trois et cette impossibilité confirme la structure « sandwich ». Pour un dérivé disubstitué du type $MA_{(1)}\ A_{(1')}\ B$ il n'existe par contre que deux isomères. (VII et VIII).

La distinction entre les dérivés disubstitués homo et hétéro peut se faire par analyse infrarouge. Tous les dérivés ayant un cycle non substitué (et en particulier les dérivés *homo*) présentent des pics à 9 et à 10 μ. Ces deux bandes disparaissent pour les dérivés hétéro. Remarquons d'autre part que certains dérivés schématisés ci-dessus peuvent donner lieu au phénomène d'isométrie optique.

— *Cycles homocondensés* — *Isomérie exo-endo.*

Si l'on considère maintenant un cycle homo condensé sur un seul noyau, on peut prévoir l'existence d'isomérie *optique* et d'isomérie *exo-endo*.

L'isomère optique a pu être mise en évidence dans le cas de la ferroco—1—2 cyclohexanone—3 (analogue de la tétralone). Cette cétone a en effet pu être dédoublée par la menthylhydrazine. (IX et X).



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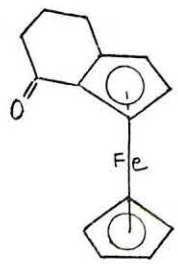
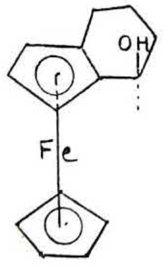


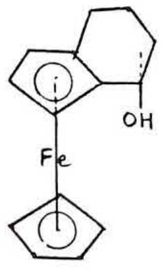
(X)

Ferroco—1,2 cyclohexanone—3



(XI)

exo



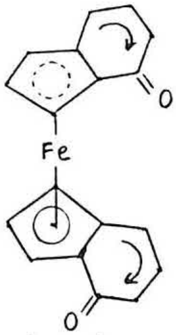
(XII)

endo

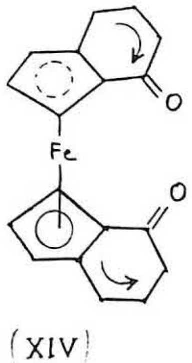
L'isomère exo-endo n'est encore connu que dans un seul cas : celui des deux ferroco cyclohexanols. (XI et XII).

Ces deux alcools s'obtiennent par réduction de la cyclohexanone par $LiAlH_4$ dans les proportions respectives de 11 % et 89 %. Evidemment chacun d'entre eux doit théoriquement être dédoublable, mais cette tentative de dédoublement n'a pas encore été faite.

Enfin il nous à été possible de préparer les deux dicétones schématisées ci-dessous. Ces deux dicétones résultent respectivement d'un enroulement dans le même sens ou en sens inverse des chaines latérales portant une fonction acide. (XIII et XIV).



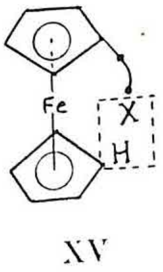
(XIII)



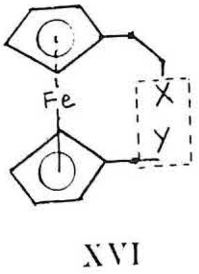
(XIV)

— *Cycles hétérocondensés.*

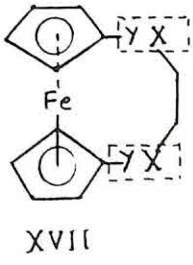
La structure « sandwich » se prête à un autre type d'isomérie. On peut en effet imaginer qu'il sera possible de joindre les deux cycles par un pont hétéroannulaire. Cette cyclisation a pu être faite par différentes voies :



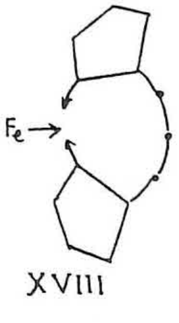
XV



XVI



XVII



XVIII

a) Cyclisation hétéroannulaire d'une chaine latérale ou réaction d'élimination entre deux chaines hétérosubstituées. (XV et XVI).

b) Double condensation d'un greffon sur un dérivé disubstitué hétéroannulaire.

c) Synthèse directe par flexion d'une chaine portant à ses deux extrémités un motif cyclopentadiène. (XVIII).

La première méthode a déjà été très utilisée. On a même réussi à faire des doubles ponts carbonés hétéroannulaires.

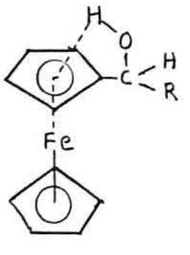
La deuxième méthode est moins commune car, si l'on excepte le diacétyl 1,1' ferrocène, on dispose de très peu de dérivés disubstitués hétéro.

Quant à la cyclisation par flexion, elle a été tentée dans quelques cas mais les rendements restent très mauvais.

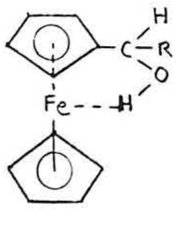
Propriétés dues à l'atome de fer

Pour terminer, nous envisageons maintenant le troisième groupe de propriétés : celles qui sont dues à l'atome de fer.

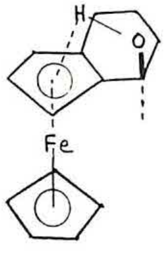
Nous trouvons tout d'abord des phénomènes de chélation.



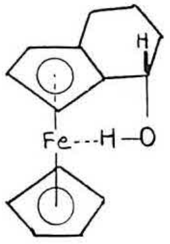
XIX



XX



XXI



XXII

Si l'on envisage un alcool dérivé du ferrocène, l'H du OH peut être chélaté soit avec les électrons π du cycle (XIX), soit avec le fer (XX). Il s'agit d'une véritable liaison hydrogène-fer. Il en résulte un déplacement considérable de la bande infrarouge caractéristique du OH. Elle passe de 3 605 cm^{-1} à 3 553 cm^{-1}. On peut attribuer l'origine de ces bandes grâce à l'étude des deux molécules modèles représentées ci-dessus. Pour le composé *exo* (XXI), on ne peut évidemment pas envisager de chélation sur le fer. Par contre, pour le composé *endo* cette possibilité existe. (XXII).

Une deuxième propriété due à l'atome de fer est *la facilité de protonation de la molécule.*

En milieu très acide le ferrocène est protonisé d'après FcH + $H^+ \rightarrow FcH_2^+$. Et on doit tenir compte de ce fait lorsqu'on opère des réactions en milieu très acide.

On attribue également à l'atome de fer une autre caractéristique de ces molécules. C'est la stabilité remarquable de l'ion $\mathrm{Fc\ CH_2^+}$. Cet ion carbonium est l'analogue de l'ion benzyl $\mathrm{C_6H_5\ CH_2^+}$ mais il est beaucoup plus stable.

On peut même dire que l'ion $\mathrm{Fc\ CH_2^+}$ est presque aussi stable que l'ion $\mathrm{(C_6H_5)_3C^+}$ qui est le type même des ions « carbonium » stables.

Ceci a une conséquence chimique : les alcools du type Fc CH OHR se déshydrateront avec la plus grande facilité car la déshydratation se fait toujours par l'intermédiaire du carbonium.

Mais la propriété la plus caractéristique du ferrocène c'est l'oxydation du ferrocène en sel de ferricinium

$$\begin{array}{ccc} \mathrm{Fc\ H} - e & \rightarrow & \mathrm{Fc\ H^+} \\ \text{orange} & & \text{bleu} \end{array}$$

Il s'agit là d'un véritable couple oxydo-réducteur réversible. Le potentiel redox est de l'ordre de + 0,30 volts.

Or on sait que les systèmes redox sont assez rares en chimie organique. L'existence de cette réversibilité présente un intérêt certain.

En effet, on peut faire varier la valeur du potentiel redox par des modifications structurales sur le squelette. Et on a ainsi réussi à obtenir toute une gamme de systèmes redox dont les potentiels varient de — 0,20 volt à + 0,80 volt environ, c'est-à-dire une gamme d'environ 1 volt.

LES DERIVES DU FERROCENE

Pour terminer nous donnerons quelques détails sur les dérivés les plus intéressants du ferrocène que nous n'avons pas encore rencontrés.

L'hydroxyferrocène et l'aminoferrocène ne peuvent être obtenus par les synthèses classiques utilisées en série aromatique.

L'hydroxyferrocène a été isolé pour la première fois par Nesmeyanov par la suite de réactions :

$$\left\{ \begin{array}{l} \mathrm{Fc\ B\ (OH)_2 + 2\ Cu\ (OCOR)_2 + 2\ H_2O \rightarrow FcO\ COR} \\ \mathrm{Fc\ OCOR + 2\ \ Mg\ Br \rightarrow Fc\ O\ Mg\ Br \rightarrow Fc\ OH} \end{array} \right.$$

L'aminoferrocène s'obtient par la réaction de Curtius ou mieux de Kotcheskov (action du lithien sur la benzylhydroxylamine)

$$\mathrm{Fc\ COCl} \rightarrow \mathrm{Fc\ CO\ N_3} \rightarrow \mathrm{Fc\ NH_2}\quad \text{(Curtius)}$$

$$\mathrm{Fc\ Li} + \mathrm{C_6H_5CH_2\ O\ NH_2} \rightarrow \mathrm{Fc\ NH\ Li} \rightarrow \mathrm{Fc\ NH_2}$$

(Kotcheskov)

Cette amine donne les mêmes dérivés caractéristiques que l'aniline mais il est impossible de la diazoter. Cette impossibilité est certainement due à une oxydation préalable du ferrocène par NO_2H.

C'est également à partir du lithien que l'on obtient l'acide par carbonatation. Mais là encore on a intérêt à utiliser des méthodes originales.

En effet, dans la préparation du lithien, on obtient toujours un mélange de dérivé mono et disubstitué et la séparation des deux acides qui en résultent est délicate. De plus la méthode ne peut être généralisée car l'organo métallique peut réagir sur les groupements fonctionnels préexistants. On a signalé récemment une méthode générale permettant d'accéder au seul dérivé monosubstitué. C'est la réaction du chlorure de carbamyle (ou de diphénylcarbamyle) selon Friedel et Crafts. On obtient l'amide qu'il suffit d'hydrolyser.

$$\mathrm{FcH} + \mathrm{H_2N\ COCl} \xrightarrow{\mathrm{AlCl_3}} \mathrm{Fc\ CO\ NH_2} \longrightarrow \mathrm{Fc\ CO_2H}$$

Il est intéressant de comparer les propriétés acido basiques des dérivés du ferrocène à ceux du benzène. On a trouvé, dans les mêmes conditions expérimentales :

		pK_B
C_6H_5	NH_2	10,14
Fc	NH_2	8,81

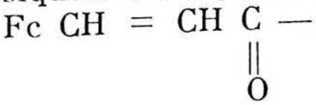
		pK_A
C_6H_5	CO_2H	6,32
Fc	CO_2H	6,78

L'aminoferrocène est donc une base plus *forte* que l'aniline et l'acide ferrocènecarboxylique un acide légèrement plus faible. Ce résultat montre encore le caractère nucléophile ou plutôt l'électropositivité du ferrocène par rapport au benzène.

Cette électropositivité de Fc se retrouve si l'on compare quelques autres valeurs de la littérature, par exemple :

			pK_B
C_6H_5	(p)	$C_6H_4\ NH_2$	10,89
Fc	(p)	$C_6H_4\ NH_2$	7,66

			pK_A
C_6H_5	(p)	$C_6H_4\ OH$	11,05
Fc	(p)	$C_6H_4\ OH$	11,80

Parmi les autres dérivés intéressants, nous trouvons évidemment le ferrocénaldéhyde. Cet aldéhyde est assez stable à l'oxydation et présente de légères propriétés basiques. On a pu en préparer toute une série de chalcones  $\mathrm{Fc\;CH = CH\;\underset{\overset{\|}{O}}{C} - R}$ et il peut être réduit normalement en alcool.

L'acétylferrocène est probablement l'un des composés les plus connus. Il s'obtient selon Friedel et Crafts et sert de départ à la préparation de nombreux composés en particulier FcC_2H_5 par réduction selon Clemmensen.

On connait également Fc CH_2 et on a étudié le vinylferrocène Fc $CH = CH_2$.

Dans ce même ordre d'idées, on a signalé récemment la préparation du ferrocénylbutadiène.

On envisage actuellement d'utiliser ces derniers composés comme précurseurs de polymères présentant dans leurs molécules des atomes métalliques.

Cette dernière remarque pose le problème de l'utilisation éventuelle de ces nouvelles molécules à des fins industrielles.

Les applications restent encore très limitées. Certains « sandwich » dérivés du mangasène ont été proposés comme antidétonants. Les dérivés du ferrocène ont été utilisés comme protecteurs des matériaux plastiques exposés à la détérioration photochimique. On peut également penser que la thermolyse de telles molécules pourra engendrer des résidus métalliques intéressants dans le domaine de la catalyse.

Section 9 Models and experiments

Chemistry is an experimental science, and it is of immense importance that the imagination of the young student should be stimulated by doing experiments, making informed observations and drawing conclusions from these observations. Some experiments require expensive equipment or facilities not available in the school laboratory, and it is in this field that aids such as films and television have such a vital role to play. It is hoped that a subsequent edition of "New Trends" will include an account of progress in this field (see page 350 of this edition for a reference to some successful programmes on chemistry teaching in Hungary). Fortunately, there are very many informative experiments that do not need elaborate or expensive equipment, and a small selection of these is included here.

Most college chemistry courses in recent years have introduced instrumental methods to a greater or less extent in their laboratory programmes. The scheme outlined by S. E. Wiberley and H. H. Richtol is typical of many such programmes and the details may be helpful to those planning courses on these lines. See also the interesting list of experiments to accompany a course on valency and structure on page 39.

An adequate grasp of modern structural chemistry can be achieved only by making and handling models of molecular or crystal structures. The article by K. S. Tetlow contains a great deal of practical information which will save any teacher starting to make models in expanded polystyrene a great deal of time. There is a useful working drawing for the construction of a jig for the rapid construction of "tetrahedral" carbon atoms.

Reprinted from *Chemistry*, Vol. 37, No. 4, 1964, p. 27.

How Large is a Molecule?

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In physics and chemistry courses we learn that matter consists of minute particles which we call molecules. In the case of a gas—for instance oxygen—we must assume that within it the oxygen molecules fly around at random at great speed, like a swarm of mosquitoes. Liquids also—water, for example—are composed of molecules; these make contact with each other. They admittedly can move past each other, but they remain in contact so that together they form a definite volume. In solids we must think of the molecules as bound to a particular place; for this reason a solid body has a fixed shape and a definite volume.

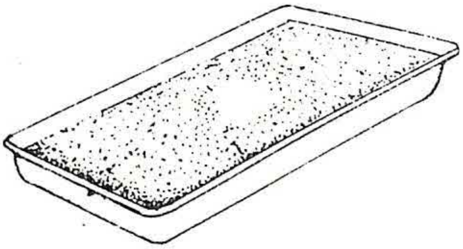
Let us imagine for simplicity that molecules are small spheres. A logical question then is: "How large is a molecule in reality?" In our books one can find the answer: Depending on the number of atoms that are united in a molecule, the diameter of the molecule comes to 10^{-8} to 10^{-7} cm. And readers with a thirst for knowledge may ask: "Can this magnitude be determined experimentally?"

A simple experiment together with a calculation permits us in fact to determine the order of magnitude of the diameter (d) of a given molecule.

If a small drop of oil is placed on water, the oil spreads to a relatively large, almost circular spot. If we assume that this surface consists of only *one* layer of oil molecules (for which, as we will see later, we have a certain amount of justification), then this material will be in the form of a very flat cylinder whose height is equal to diameter d of the molecule. The limits of the cylinder can be made visible by means of lycopodium powder; it is pushed back by the spreading oil. That quantity of oil which will produce a circular area 20 cm. in diameter is so small that it cannot be weighed without balances; yet it can be determined.

Wheat flour contains about 1% of oil by weight. (This has been determined by extracting it from 1 kilogram of flour by means of benzene which absorbs the oil). The oil has a density of 0.9 gram per cubic centimeter (cc.) If, for instance, 0.003 gram of flour is weighed out on the analytical balance, this quantity contains 0.00003 gram of oil, which is just sufficient for our experiment.

The experiment is carried out as follows: A carefully cleaned (with all fat removed) serving tray (about 35 × 40 cm.) is filled with water. When the liquid has come to rest, lycopodium powder is spread as uniformly as possible in its center to a circular area of 8 to 10 cm. diameter. After a minute, when no more motion is visible on the water, 0.003 gram of flour is allowed to fall into the center of the lycopodium powder. Immediately a clear surface is formed by the spreading oi which pushes the powder in front o it. The clear surface grows for one or two seconds. But when it reaches a diameter of about 20 cm. no further increase can be observed. Now the diameter is measured ($2r$). In our calculation we will assume that it is exactly 20 cm., so that $r = 10$.



Calculation

Mass of oil = 0.00003 gram

$$\text{Volume of oil} = \frac{0.00003}{0.9} = 0.000033 \text{ cc.}$$

$$\text{Volume of cylinder} = \pi r^2 d = \pi 10^2 d = \pi 100 d \text{ cc.}$$

From this we obtain $\pi 100\text{d} = 0.000033$ cc.

$$d = \frac{0.000033}{100\pi} = 0.00000011 \text{ cm.}$$

This result, understandably, can represent only an approximate value; however, it does correspond to the *order of magnitude* of the values given in textbooks.

In experiments with different quantities of oil, the result remains approximately the same. Therefore, one may assume that the spread of oil on water is limited by molecular size—that is, the layer of oil has the thickness of a molecular diameter.

In conclusion, we mention one other method of obtaining the minute quantity of oil needed—preparing a highly diluted solution of oil in petroleum ether of known concentration. From this solution one allows a suitable quantity—measured in 0.1-cc. pipet— to drop onto the water. The solvent evaporates immediately.

Reprinted from *Chemistry*, Vol. 37, No. 4, 1964, pp. 24-25.

Stoichiometry of the Mercury(II) Nitrate–Potassium Iodide–Water System

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LAB BENCH

A student was given the problem of investigating the stoichiometry of the mercury(II) nitrate–potassium iodide–water system. Before beginning her experimental work, she consulted the literature to obtain information on her system. She found that a solution of mercury(II) nitrate can be prepared easily if a small quantity of nitric acid is present. The reaction of mercury (II) ion with iodide ion was reported to form mercury(II) iodide, a slightly soluble salt with a solubility product constant of 1.51×10^{-24} (*4*). She also discovered that under some conditions a complex ion (*1*) would form while under other conditions an ion-pair (*4*) would form. On the basis of this information, she decided to conduct her investigation to obtain data usable for considering the composition requirements of the system for the formation of mercury(II) iodide, the complex ion, and the ion pair.

Continuous variation experimental design was selected for the investigation. This design (*2*) involves a series of determinations in which the quantities of the two reactants are varied in such a way that in each determination the sum of the quantities of the two reactants always equals a constant value. As the quantity of one of the reactants is increased in the series of determinations, the quantity of the other reactant is decreased by a corresponding amount. The quantities of the reactants can be expressed in units of volume, mass, or moles. To find the effect of varying the quantities of reactants on the system, the magnitude of some property of the system is determined. Mass, volume, and temperature are examples of properties that are frequently measured. By plotting the magnitude of the property of the system against the quantities of reactants, the effect of the quantities of reactants on the system can be determined from the shape of the resulting curve. Any maximum point on the curve would identify specific stoichiometric relationships in the system, indicating the composition that gives the maximum reaction.

Because mercury(II) iodide is slightly soluble in water, the student decided to determine the mass of mercury(II) iodide formed and, in addition, to calculate the density of the liquid phase of the reaction mixture from mass-volume data. By plotting the quantity of mercury(II) iodide or the density of the liquid phase of the reaction mixture against the quantities of reactants used, she reasoned that she could obtain information about the stoichiometry of the reaction.

For her investigation of the mercury(II) nitrate–potassium iodide–water system, she prepared a 1.0*M* potassium iodide solution and a 0.5*M* mercury(II) nitrate solution. The mercury(II) nitrate solution was prepared by adding 0.5 mole of solid mercury(II) nitrate to 500 ml. of distilled water to which 20 ml. of concentrated nitric acid was added. When the solution cooled to 20° C., it was diluted to 1 liter in a volumetric flask. Quantities of reactants used are given in Table I.

LAB BENCH presents its second report on student research (see CHEMISTRY, *January 1964, page 29). Experimental extensions of these data, interpretations, and answers to the questions will be considered by the editors for publication.*

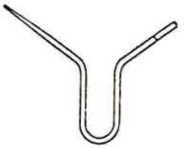
TABLE I. Experimental Data for Investigating the Mercury(II) Nitrate–Potassium Iodide–Water System

Assignment No.	Quantities of Reagents Used: 1.0*M* KI, ml.	Quantities of Reagents Used: 0.5*M* $Hg(NO_3)_2$, ml.	Mass of Residue HgI_2, grams	Density, Liquid Phase of Reaction Mixture, grams/ml.
1	0.00	20.00	0.00	1.142
2	1.00	19.00	0.00	1.136
3	2.00	18.00	0.10	1.132
4	4.00	16.00	0.63	1.106
5	6.00	14.00	1.14	1.082
6	8.00	12.00	1.67	1.057
7	10.00	10.00	2.24	1.031
8	11.00	9.00	1.75	1.044
9	12.00	8.00	1.04	1.076
10	13.00	7.00	0.34	1.102
11	14.00	6.00	0.00	1.118
12	16.00	4.00	0.00	1.116
13	18.00	2.00	0.00	1.114
14	20.00	0.00	0.00	1.115

PROCEDURE

A description of the procedure that the student used for her investigation follows: The assigned volumes of 1.0*M* potassium iodide and 0.5*M* mercury(II) nitrate were measured from a buret into labeled 20 mm. × 150 mm. test tubes. The test tubes were stoppered. The tubes and their contents were thoroughly shaken and placed in a constant temperature bath held at 25° C. After about 20 minutes—the time required for test tubes and their contents to equilibrate in the water bath—the mixtures were filtered using dry, tared qualitative filter papers. The filtrates were collected in labeled 20 mm. × 150 mm. test tubes, which were stoppered and placed in the constant temperature bath. The residues were washed on the filter papers three times with small portions of distilled water and were dried in an oven at 110° C. for $1^1/_2$ hours. They were allowed to cool overnight, and the masses were determined. The densities of the liquid phase of the reaction mixtures were calculated from mass-volume data obtained with a glass capillary tube pycnometer (*3*) using a Mettler balance for mass measurements.

Pycnometer for density measurements
If made from 3-mm. glass tubing, the pycnometer has a capacity of 0.2 to 0.4 ml.; made from melting point capillary tubing, the capacity is 0.02 to 0.03 ml.



DATA PROCESSING

The student calculated the number of moles of reactants and the number of moles of mercury(II) iodide formed for each of the assignments studied. These data were used to prepare two graphs. In one, the density of the liquid phase of the reaction mixture was plotted against the number of moles of reactants. Along the abscissa, the number of moles of potassium iodide increased from 0 to 20 × 10^{-3}, while the moles of mercury(II) nitrate decreased from 10 × 10^{-3} to 0.

On the second graph, she plotted the number of moles of mercury(II) iodide formed against the number of moles of reactants used. On this graph she also plotted the curve which represented the theoretical number of moles of mercury(II) iodide that would be formed on the basis of the quantity of the limiting reagent, assuming the reaction went to completion.

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QUESTIONS

1. Of what significance is the shape of the curve obtained when the density of the liquid phase of the reaction mixture is plotted against the number of moles of reactants? What information can be obtained from this graph about the composition of the system when (a) mercury(II) iodide is formed, (b) a complex ion is formed, and (c) an ion pair is formed?

2. In the plot of the experimentally determined number of moles of mercury(II) iodide against the number of moles of reactants, (a) what does the stoichiometric point indicate about the system? (b) What explanation can be offered for the shape of the curve for the experi*mental number of moles of mercury(II) iodide as compared to the shape of the curve for the* theoretical *number of moles of mercury(II) iodide?*

3. Mercury(II) iodide can exist in equilibrium with the liquid phase of the reaction mixture if the ion product, $[Hg^{2+}]\,[I^-]^2$, is equal to the solubility product constant, K_{SP}. (a) In what regions of the graph is the ion product less than the K_{SP}? (b) How do you account for these facts?

4. At what mole ratio of iodide ion to mercury(II) ion does the maximum number of moles of complex ion form? What is the equation for complex formation based on this mole ratio?

5. At what mole ratio of iodide ion to mercury(II) ion does the maximum number of moles of ion pair form? What explanation can be offered for the difference between the effect of complex ion formation on the solubility of mercury(II) iodide and the effect of ion-pair formation on the solubility of mercury(II) iodide?

6. Would any significant information about the mercury(II) nitrate–potassium iodide–water system be obtained from a thermochemical investigation of the system using a continuous variation experimental design? What experimental procedure could be used for such a study? How would the data be processed so that they could be used to consider the effect of composition on the nature of the system?

7. Could an electrolytic cell be constructed that could be used to investigate the effect of composition on the mercury(II) nitrate–potassium iodide–water system? Would there be any advantage in doing an electrical conductivity study of the system?

8. What experimental evidence can be obtained to show whether ion pairs and complex ions exist in a mercury(II) nitrate–potassium bromide–water system?

9. How does ion-pair and complex-ion formation in the mercury(II) ion–halide ion systems compare with ion-pair and complex-ion formation in the lead(II) ion–halide ion systems?

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A Simple Quantitative Electrolysis Experiment for First Year Chemistry

Most freshman chemistry laboratory courses include work in electrochemistry, usually an experiment in electrode potentials and one in electrolysis. The commonly employed electrolysis experiments tend to be of two types. Some are intended simply to illustrate the nature of electrode reactions through the appearance of electrode products, e.g., I_2 which is detected by its color, OH^- which is detected with phenolphthalein indicator, and H_2 and O_2 which are collected as gases (*1–5*). Other experiments are designed as quantitative illustrations of Faraday's laws and usually involve a comparison of the electrochemical change occurring at an electrode with the corresponding change occurring in a coulometer, these comparisons being made on a weight basis (*6–8*). Recently a number of electrolysis experiments illustrating the principles of coulometry have been described (*9, 10*).

The requirements we have imposed in our selection of an electrolysis experiment for freshman chemistry is that it be simple to perform, that the equipment required be inexpensive (less than $10 per student set-up), and that a quantitative application of Faraday's laws should be possible in the experiment, but without the need for analytical balances.

The Experiment

The electrolysis employed is that of 0.5 *M* Na_2SO_4 solution. Two 400-ml beakers serve as half-cell compartments. To provide maximum contact between electrodes and solution, and to immobilize the electrodes, we have found it advantageous to use metal foil electrodes which are contour-fitted to the bottom and walls of the beakers. To each compartment is added 200 ml of 0.5 *M* Na_2SO_4. A 10.0-ml sample of an H_2SO_4 solution of about 0.001 to 0.01 *M* is pipetted into the cathode compartment. The acid solution is provided as an "unknown." Four drops of an appropriate indicator are added to the cathode compartment. The electrodes are connected to a milliammeter and two 6-v dry cell batteries connected in series. The circuit is closed by joining the two half-cell compartments with a U-tube filled with agar gel which is impregnated with 0.5 *M* Na_2SO_4.

The experiment is timed by using either a stop watch or the sweep second hand of a wrist watch or wall clock. The current is measured as a function of time, and the length of time required to produce a color change in the cathode compartment is noted. The end point is best approached by interrupting the current by removing the salt bridge, stirring the solution in the cathode compartment and noting the indicator color. The salt bridge can then be replaced for short periods (about 5 sec) until the exact end point is reached.

We have found that good results are obtained with the student set-ups if the solution in the cathode compartment is stirred intermittently. Stirring is helpful in locating the end point of the neutralization reaction. However, if a more precise milliammeter is used in the experiment the best results are obtained when the solution in the cathode compartment is not stirred until just prior to the end point. This is because of the tendency for stirring to partially depolarize the electrodes. The current remains practically constant if the electrodes are polarized during the electrolysis.

Details

The Half-Cell Reactions. If the electrodes used in the electrolysis are inert the overall reaction is simply the electrolysis of water, occurring as the two half-reactions,

$$\text{Anode: } 2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
$$\text{Cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

The OH^- produced at the cathode neutralizes the H^+ in the acid sample added to the cathode compartment.

A Typical Run. Some typical data obtained in the coulometric analysis of 10.0 ml of an unknown H_2SO_4 solution are presented in Table 1. The total amount of electrical charge involved in the electrolysis is determined by summing together a number of increments. If desired this charge can be determined by plotting current as a function of time and evaluating the area under the curve. We have found the summation of increments to be quite satisfactory. The final result has been rounded off to suggest an accuracy of analysis of about 1%. The accuracy is limited primarily by the accuracy of the milliammeter.

Indicator and Indicator Blanks. In 0.5 *M* Na_2SO_4 solutions prepared from ordinary distilled water, an appreciable quantity of dissolved CO_2 is present. This means that in an analysis not only must the unknown acid be neutralized in the cathode compartment, but also carbonic acid. There are two ways to make allowances for dissolved CO_2. In one method an indicator blank is run on 200 ml of 0.5 *M* Na_2SO_4 in the cathode compartment. The blank must then be subtracted from the experimental value obtained with the unknown acid (see Table 1). In the second method the 200 ml of 0.5 *M* Na_2SO_4 is pre-electrolyzed until the indicator in the cathode compartment assumes its basic color. The unknown acid is then added and electrolysis resumed until this same color change is produced for a second time.

Many different indicators have been used in this experiment and a number of them have proved satisfactory. Phenol red, phenolphthalein, and bromthymol blue are all quite suitable. It is instructive to determine indicator blanks for several indicators and to show how the values obtained can be related to the pH range over which the indicator color change occurs. For example with bromthymol blue (pH 6.0–7.6), blank = 1.26 coulombs; phenol red (pH 6.6–8.0), blank = 1.42; phenolphthalein (pH 8.3–10.0); blank = 1.84.

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Table 1. Typical Data in the Analysis of An H_2SO_4 Unknown[a]

Time × Current	Time (min)	Time (sec)	Current (ma)	Remarks
15 × 21.8 = 327	0		22	Solution yellow
		15	21.6	" "
15 × 21.6 = 324		30	21.5	" "
30 × 21.5 = 645	1		21.4	" "
180 × 21.4 = 3860	2		21.4	" "
	4		21.4	" "
120 × 21.3 = 2560	6		21.3	" "
	8		21.2	" "
150 × 21.2 = 3180	8	30	21.2	Interrupt current, stir
	8	45	21.9	Solution yellow
				Yellow
35 × 22 = 770	9		21.8	Pink, non-lasting
	9	5	22.2	Definite lasting pink

Total = 11.666 coulombs
Blank = −1.50
10.17 coulombs

$$[H^+] = 10.17 \text{ coulombs} \times \frac{1 \text{ mole } e^-}{96{,}500 \text{ coulombs}} \times \frac{1 \text{ mole OH}^-}{1 \text{ mole } e^-} \times \frac{1 \text{ mole H}^+}{1 \text{ mole OH}^-} \times \frac{1}{0.01\,1} = 0.0106\ M$$

$[H^+]$, determined by direct titration = 0.0105 M

[a] Conditions: Two 4F dry cells (12v), Simpson 1329C, 0–25 ma meter Pt gauze electrodes, phenol red indicator (0.02%).

Salt Bridge. The following procedure works well for preparing salt bridges. Soak 12.5 g of USP grade agar in a small volume of cold water. Add to this agar 500 ml of a boiling water solution containing 0.25 moles Na_2SO_4. Carefully pour the agar solution into 6-in. U-tubes maintained in an upright position. Allow the agar to gel. Upon gelation there will be a slight contraction in volume. Add a small volume of hot agar solution to each arm of the U-tubes to fill them completely. The quantities given here are sufficient to fill about 8 U-tubes. The gels can be preserved for a rather long period of time by inverting the U-tubes in a solution of 0.5 M Na_2SO_4.

Choice of Electrodes. The electrodes chosen for the experiment should be inert; at least they should be such that the only significant cathode reaction is the reduction of water. In Table 2 are presented the results of the analysis of an H_2SO_4 solution using four different sets of electrodes. The results with all the electrodes are within the 1-2% accuracy anticipated with the milliammeter used.

It was noted that with copper and silver electrodes some oxidation of the metal to the metal ion did occur at the anode. The presence of Ag^+ was determined with Cl^- and that of Cu^{2+} using PAN indicator (1-(2-pyridyl-azo)-2-napthol). We have used copper electrodes in the student experiment, although from the standpoint of accuracy and cost, nickel electrodes would be equally satisfactory.

Table 2. Comparison of Electrodes[a]

Electrodes	$[H^+]$ found (M)
Copper	0.0075
Silver	0.0075
Nickel	0.0073
Platinum	0.0073
$[H^+]$, determined by titration	0.00738

[a] Conditions: Two 4 F dry cells (12 v), Simpson 1329C, 0–25 ma meter, phenol red indicator (0.02%).

Table 3. Typical Student Results

Student group	$[H^+]$ found	True $[H^+]$ by titration
1	0.0029	0.00321
2	0.0031	"
3	0.0032	"
4	0.062	0.0738
5	0.066	"
6	0.068	"
7	0.076	"
8	0.0102	0.0105
9	0.0104	"
10	0.0105	"

Choice of Meters. The accuracy with which the experiment can be performed is determined almost exclusively by the quality of the milliammeter used. The results presented in Tables 1 and 2 were obtained using a Simpson 1329C, 0–25 ma, dc meter. This meter, which costs about $15, could be read to the nearest tenth of a milliampere and had an accuracy rated at 2%. In the student set-ups an EMICO, 0–50 ma, dc meter, which costs less than $2, was used. With this meter, current can be estimated to 0.5 ma, at best, and the rated accuracy is only 5%. EMICO meters were chosen for the student experiment because of their lower cost.

Comparison of the two different milliammeters indicated that most of the EMICO meters give low readings, by as much as 10%. For use in student experiments one may either calibrate each of the low-cost meters against a more precise meter or apply the correction factor of roughly 10%.

Typical Student Results. Table 3 summarizes the results obtained in some typical student experiments. These results are not nearly as accurate as those presented in Tables 1 and 2 but almost without exception the inaccuracies are a result of the poorer quality meters.

Acknowledgment

The typical student results presented in this paper were obtained by the participants in the 1963–64 NSF In-Service Institute for High School Chemistry Teachers at Western Reserve University.

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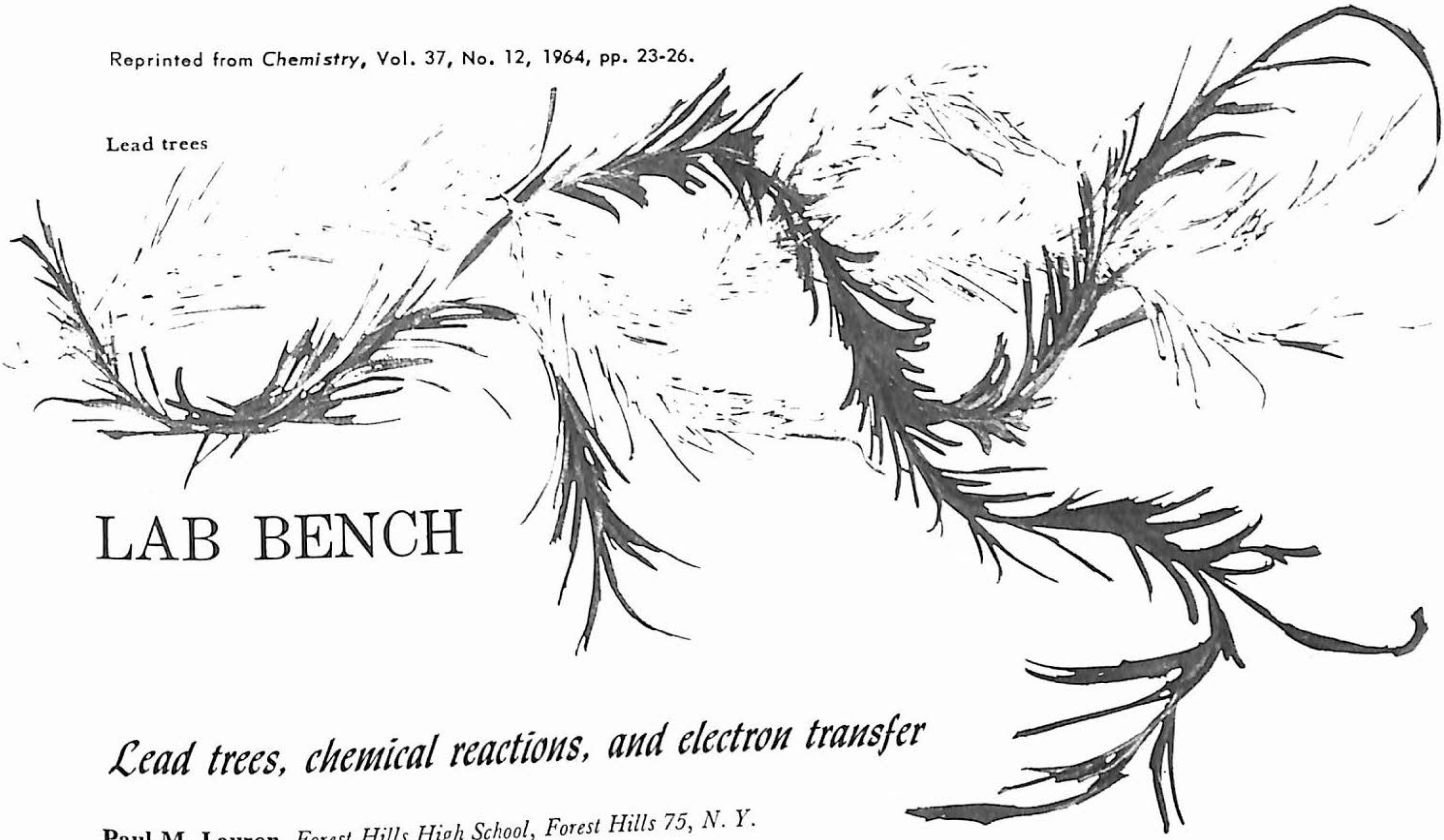

Lead trees

LAB BENCH

Lead trees, chemical reactions, and electron transfer

Paul M. Lauren, *Forest Hills High School, Forest Hills 75, N. Y.*

A lead tree is actually lead metal crystals that form during the continuous reduction of lead ions by a metal–metal ion electrode of larger positive potential than that of Pb/Pb^{+2}; for example, Zn/Zn^{+2}.

A silicic acid gel formed by acidification of sodium silicate acts as a support for the lead crystals.

Since the redox (oxidation-reduction) reaction occurs at the surface of the zinc, there must be a flow of electrons through the metal from the anode sites, where zinc atoms are oxidized, to the cathode ones where lead ions are reduced. The reactions occurring can be represented as follows:

Anode site: $Zn^0(s) \rightarrow Zn^{+2}(aq) + 2e$ $\quad E^0 = +0.76$ v

Cathode site: $Pb^{+2}(aq) + 2e \rightarrow Pb^0(s)$ $\quad E^0 = -0.13$ v

Net reaction: $Zn^0(s) + Pb^{+2}(aq) \rightarrow Zn^{+2}(aq) + Pb^0(s)$ $\quad E^0_{\text{cell}} = +0.76 - 0.13 = +0.63$ v

By observing the rate of lead crystal formation, some factors which appear to influence this redox reaction can be examined.

How Does the Concentration of the Oxidizing Agent (Pb^{+2}) Influence the Rate of Lead Tree Growth? According to Le Chatelier's theorem, decreasing the lead ion concentration will cause the equilibrium,

$$Zn^0(s) + Pb^{+2}(aq) \rightleftharpoons Zn^{+2}(aq) + Pb^0(s)$$

to shift to the left. The result should be a decrease in the rate of lead crystal formation. The expression below enables us to determine the potential of the cell as a function of the effective concentration of reactants and products at 25° C.:

$$E_{\text{cell}} = E^0_{\text{cell}} - (0.059/n) \log (\text{products}/\text{reactants})$$

where E is voltage of the cell and E^0, voltage of the cell when the effective concentrations are 1 molal and the gas pressures are 1 atm. The letter n represents the number of faradays needed to accomplish the change expressed by the equation. This relationship becomes $E = (+0.63) - (0.059/2) \log (Zn^{+2}/Pb^{+2})$ volts for this reaction.

If the lead ion concentration is decreased, size of the second term becomes larger. Since a large number is subtracted from E^0, cell potential E becomes smaller.

We can see that the rate of lead crystal growth appears to be directly proportional to the magnitude of the cell potential. When the lead ion concentration is decreased, the rate of lead tree formation should also diminish.

To test this hypothesis, three different gel mixtures were added to separate test tubes. Each solution varied only in the initial concentration of lead nitrate. These concentrations were $1.0M$, $0.1M$, and $0.01M$. After gelation, a cleaned zinc metal strip was inserted until it was entirely submerged just

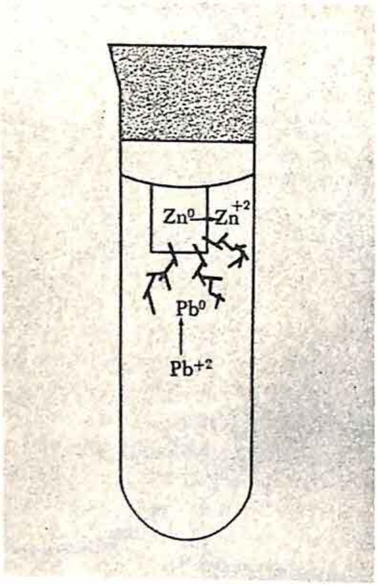

Figure 1. Lead tree formation. The tree is lead metal crystals formed by reduction of lead ions by a metal such as zinc

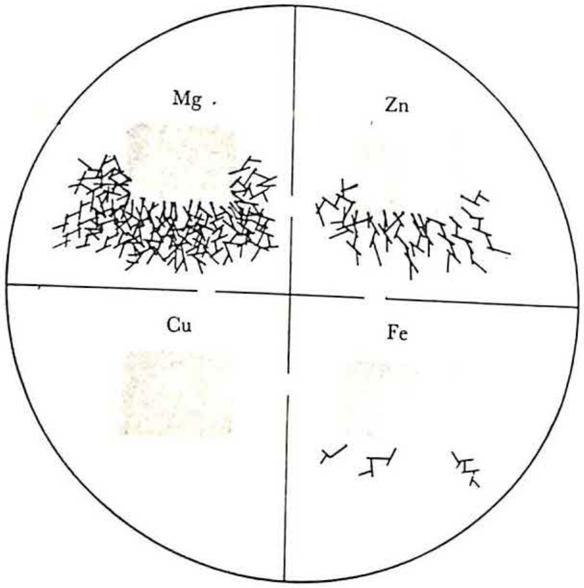

Figure 2. A Petri dish containing gel is divided into equal quadrants, each containing a metal strip. Rate of crystal formation depends on electrode potential of the displacing metal

below the surface of the gel (Figure 1). Within 2 hours it was apparent that the rate of lead tree growth varied directly with the concentration of the lead ion.

What Is the Relationship Between the Magnitude of the Electrode Potential of the Reducing Agent and Rate of Lead Crystal Growth?

Reducing Half Cell	E^0	Redox Reaction	Standard Potential for Reaction
$Mg^0 \rightarrow Mg^{+2} + 2e$	+2.37 v	$Mg^0 + Pb^{+2} \rightarrow Mg^{+2} + Pb^0$	$E^0_{cell} = +2.37 - 0.13 = +2.24$ v
$Zn^0 \rightarrow Zn^{+2} + 2e$	+0.76 v	$Zn^0 + Pb^{+2} \rightarrow Zn^{+2} + Pb^0$	$E^0_{cell} = +0.76 - 0.13 = +0.63$ v
$Fe^0 \rightarrow Fe^{+2} + 2e$	+0.44 v	$Fe^0 + Pb^{+2} \rightarrow Fe^{+2} + Pb^0$	$E^0_{cell} = +0.44 - 0.13 = +0.31$ v
$Cu^0 \rightarrow Cu^{+2} + 2e$	−0.34 v	$Cu^0 + Pb^{+2} \rightarrow Cu^{+2} + Pb^0$	$E^0_{cell} = -0.34 - 0.13 = -0.47$ v

Because the rate of lead crystal formation is related to the magnitude of the redox potential, we would predict for the reactions tabulated above that the most rapid growth should occur if magnesium were used. Zinc and iron would be intermediate. Copper should produce a negative result. This idea was examined using a gelling solution prepared with 1.0*M* lead nitrate.

The mixture was poured into a Petri dish of 9-cm. inner diameter (Fisher Catalog 8-754). The gel was cut into approximately equal quadrants. A cleaned metal strip of equivalent surface area was inserted, on edge, into each quarter (Figure 2).

After 2 hours, it could be easily seen that the rate of lead crystal formation varies directly with the magnitude of the half-cell oxidation potential of the reducing agent.

Is It Possible to Show That a Flow of Electrons Occurs During the Formation of the Lead Tree?

In order to show that there was a flow of electrons, the cathode site must be transferred away from the surface of the reducing metal.

Since part of the reducing metal's surface must act as a cathode, there is less metal available to undergo oxidation. If more zinc atoms could be oxidized, it seemed reasonable to suppose that the rate of lead tree growth might increase. To study this problem, a strip of zinc was attached to one of copper by means of a copper wire (Figure 3).

With this arrangement, both metal strips could be stood on edge, about 5 cm. apart, in a Petri dish. The dish held a silicic acid gel prepared with 1.0*M* lead nitrate (Figure 4).

After a half hour, needles of lead appear on the surface of both the zinc and the copper. However, by the end of the second hour, the lead crystal growth from the surface of the copper predominates. The lead tree now grows faster from the surface of the copper than it did when zinc alone had been used.

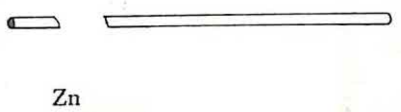

Figure 3. The end of the wire is threaded through the two holes in the metal strip. The edge of the metal strip is then folded over the wire

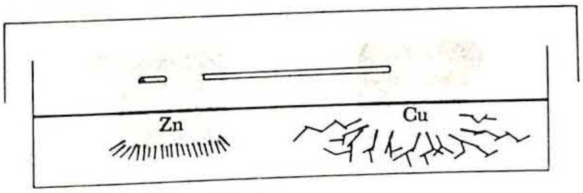

Figure 4. When copper and zinc strips about 5 cm. apart are stood on edge in the Petri dish, lead crystal formation from the copper surface predominates

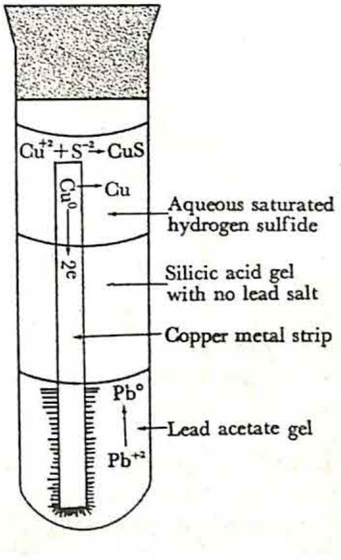
Cu+2+S-2→CuS
Cu
Cu0
2e
Aqueous saturated hydrogen sulfide
Silicic acid gel with no lead salt
Copper metal strip
Pb°
Lead acetate gel
Pb+2

Figure 5. Precipitation of CuS displaces equilibrium in the Cu/Cu^{+2} half cell toward oxidation of copper ions by lead ions

How Can a Redox Equilibrium Be Displaced So That a Half Cell of Low Standard Oxidation Potential Is Able to Reduce One of Larger Positive Value? We have seen that under ordinary experimental conditions copper atoms will not be oxidized by lead ions.

$$Cu^0 \rightarrow Cu^{+2} + 2e \qquad E^0 = -0.34 \text{ v}$$

$$Pb^0 \rightarrow Pb^{+2} + 2e \qquad E^0 = +0.13 \text{ v}$$

This means that the reaction $Pb^{+2} + Cu^0 \rightarrow Cu^{+2} + Pb^0$ cannot normally occur.

The Le Chatelier theorem predicts that copper atoms can be made to reduce lead ions if the free cupric ion concentration is decreased sufficiently to displace the equilibrium to the right. The addition of sulfide ions should diminish the cupric ion concentration tremendously:

$$Cu^{+2} + S^{-2} \rightarrow CuS(s) \qquad K_{sp} = 8 \times 10^{-36}$$

The expression for cell potential E of the redox reaction is

$$E_{cell} = -0.47 - (0.059/2) \log (Cu^{+2}/Pb^{+2})$$

If the cupric ion concentration is decreased, the ratio (Cu^{+2}/Pb^{+2}) becomes smaller. The negative logarithm of this number will be large and positive. When it is added to E^0, the answer for the calculated cell potential E must also be positive. This means that the reaction should take place.

With a technique pioneered by Taft and Stareck (*4*), the following experiment was performed. One third the volume of a test tube was filled with a gelling solution using 1.0*M* lead nitrate. After this solution had gelled, an equal volume of acidified sodium silicate without lead salt was added. Prior to gelation, a clean narrow strip of copper was inserted through both gel layers. The metal was of sufficient length to protrude through the upper surface of the second gel (Figure 5). When this second layer had gelled, a volume of aqueous saturated hydrogen sulfide, approximately equal to one quarter that of the test tube, was added. This solution was made alkaline with a few drops of 10*M* sodium hydroxide. The corked test tube was inverted periodically.

Within 15 minutes, lead crystal whiskers were observed on that portion of the copper metal strip extending into the lead acetate gel.

How Are Lead Acetate Gels Prepared? Commercial 40° Baumé water glass (density 1.39) was diluted to a density of 1.06. A rigid gel formed when this solution was in turn acidified with an equal volume of 1*M* acetic acid (*1–4*). The following volume ratio was used—1:10:10 of lead nitrate, acetic acid (1*M*), and sodium silicate (density 1.06).

The lead nitrate solution is added to the acetic acid. This solution is then mixed with the diluted sodium silicate. The resultant mixture is acid to litmus. It gelled within 8 hours.

Questions

1. How does the rate of lead tree growth vary with time? Does the nature of the reducing agent influence the shape of the growth curve? Is the Pb^{+2} ion concentration important?

2. What effect does density of the sodium silicate solution used have on the rate of lead crystal formation? Can other acids be used? Is anion size or charge type important? What is optimum pH for the redox reaction? For gelation?

3. What effect does the rigidity of the gel have upon the rate of lead crystal growth? Is it possible to control the viscosity of the gel? Would the use of a different gel be advantageous?

4. Does temperature influence lead crystal growth? How could temperature effects on the redox reaction be distinguished from those due to changes in the structure of the gel?

5. Could the oxidation potential of a Fe/Fe^{+3} half cell be altered using a complexing agent such as KCNS? How might an amalgam be used to reduce lead ions?

6. Is it possible to use a sequestrant or ion exchange resin to displace a redox equilibrium? How might these materials be used to reverse the direction of electron flow in a Daniell cell?

7. Does the earth's gravitational field influence the rate of lead crystal growth? How could centrifugal force be used to modify this growth rate?

8. How could reducing agents other than metals be used to produce lead crystals? Could a d.c. power source be used?

9. Heated junctions of dissimilar metals generate an electron flow. Can a thermocouple be used as a reducing agent? Is it possible to use a photoelectric cell in a similar manner? Could sunlight be used to grow lead trees?

10. Can other metal crystals be grown in gels? (The author will send a copper tree recipe to interested students.)

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(2) Holmes, H. N., "Introductory Colloid Chemistry," p. 89–90, Wiley, New York, 1934.
(3) Holmes, H. N. "Laboratory Manual of Colloid Chemistry," 2nd ed., p. 136–9, Wiley, New York, 1928.
(4) Taft, R., Stareck, J., *J. Chem. Educ.* 7, 1520 (1930).

Reprinted from *Bulletin de l'Union des Physiciens*, 1964, pp. 788-789.

Chaleur de neutralisation de l'acide phosphorique

Neutralisation

Dans une première manipulation, on peut réaliser d'une part le dosage volumétrique classique, d'autre part suivre au PHmètre la neutralisation de l'acide phosphorique. (Le PHmètre Picoux suffit à donner l'allure du phénomène.) Dans un cas, comme dans l'autre, la troisième acidité ne peut être déterminée quantitativement.

L'expérience proposée permet de mettre en évidence les trois acidités de l'acide phosphorique. Le principe en est évident. Sur le plan pratique, les résultats sont satisfaisants en opérant de la façon suivante :

Dans un thermos à large col on introduit 300 cm^3 de H_3PO_4 N/2. On verse à l'aide d'une burette 50 cm^3 de soude 4N, de 3 en 3 ou de 4 en 4 cm^3. Après chaque addition, on note la température : un thermomètre 35° au 1/5° avec loupe de lecture suffit. Un agitateur électrique facilite la rapidité de l'opération qui est importante. Dans ce cas, il est commode d'utiliser une burette avec tube de caoutchouc et pince qui permet d'excentrer la burette et laisser la place de l'agitateur.

L'élévation totale de température est un peu inférieure à 5°. On trace le graphique des variations de température avec le volume de soude versé. On obtient quatre segments de droites de pente décroissante dont les intersections donnent les points de neutralisation. Il convient d'effectuer le tracé avec soin, particulièrement pour les points pouvant suivre de près la fin de neutralisation d'une acidité, et qu'il faut affecter à la droite suivante. Les trois volumes correspondant aux trois acidités sont trouvés égaux aux incertitudes près.

Valeur en eau

Le calcul des chaleurs de neutralisation demande la connaissance des valeurs en eau du calorimètre, des accessoires et des solutions.

On peut en faire l'objet d'une partie d'une séance de travaux pratiques de calorimétrie. En soudant les deux extrémités d'une résistance électrique à deux fils de cuivre et en la faisant pénétrer dans une gaine isolante de plastique, on peut constituer une résistance utilisable pour échauffer les 300 cm³ d'acide, puis dans les mêmes conditions 300 cm³ d'eau. Un accumulateur de 6 V et une résistance de l'ordre de 2,5 Ohms donneront un rythme d'échauffement analogue à celui de l'expérience de neutralisation.

On peut aussi admettre que la chaleur volumique des solutions est voisine de 1 cal/cm³/deg. L'approximation est moins bonne pour la solution concentrée de soude, mais le volume utilisé en est relativement faible. Pour déterminer la valeur en eau du calorimètre et des accessoires, on y place 50 cm³ d'eau environ, qui permettent de mieux déterminer la température initiale et dont la masse exacte est déterminée par double pesée. Dans un bécher, on a placé au préalable de l'eau et de gros glaçons. On agite et on note la température d'équilibre. On verse alors rapidement 200 à 250 cm³ de cette eau dans le calorimètre en arrêtant les glaçons. On note la température finale et on détermine le poids d'eau ajoutée. La discussion de l'incertitude montre que l'on s'est placé dans les conditions les plus favorables, et, à l'usage, les fautes opératoires des élèves semblent moins fréquentes par ce procédé.

Résultats

Les trois volumes n_1, n_2, n_3, sont sensiblement égaux, et on peut comparer aux dosages volumétriques préalables.

Le calcul des chaleurs de neutralisations est possible, on écrira par exemple avec des notations évidentes :

$$Q_2 = [\ (300 + \mu + n_1)\ (\Theta_2 - \Theta_1) + n_2\ (\Theta_2 - \Theta_0)\ ]\ 20$$

si la solution d'acide phosphorique peut être considérée comme N/2.

Les résultats trouvés sont voisins de 14,9, 12,3, 7,5 kcal/mole, valeurs données par Gallais et Rumeau pour les solutions M/300. Je n'ai pas eu le temps de chercher d'autres références, et, si un collègue pouvait m'en indiquer, je serais curieux de savoir les valeurs admises pour les solutions plus concentrées, ainsi que pour les chaleurs massiques ou volumiques des solutions utilisées.

J.L. ROBIN (Montréal).

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A Simple Kinetic Investigation of an Organic Reaction Mechanism

Inherent in the trend toward a more mechanistic approach in the teaching of undergraduate organic chemistry is the desire to introduce mechanistic thinking into the laboratory experiments.

Although it is realized that simple preparative reactions are extremely valuable for teaching basic laboratory skills, many such experiments can be carried through successfully without compelling the student to consider the details of the transformations that are taking place. The following kinetic experiment, which was designed for an undergraduate organic laboratory section, allows the student to determine what factors affect the rate of a reaction[1] and how this information can be rationalized in terms of a logical sequence of molecular events.[2]

The hydrolysis of *tert*-butyl chloride was chosen for a number of reasons. The reaction, as far as it is covered in an undergraduate course, involves basically simple concepts. Students are generally introduced to alkyl halides and their reactions relatively early in the first semester of most organic chemistry courses. The reaction is very easy to follow and has a convenient half-life in a properly chosen solvent system. If it is desired, the *tert*-butyl chloride can be readily prepared by the student according to procedures which appear in nearly every organic laboratory manual.

Measurement of the Rate

One of the primary features of the experiment is its fundamental simplicity. The entire experiment can be performed with only two 25-ml Erlenmeyer flasks, a 5-ml graduated cylinder (a pipet could be substituted), a 1-ml and a 5-ml graduated pipet, and a watch or clock with a second hand. The student should be provided with a 0.1 M solution of *tert*-butyl chloride in acetone, a 0.1 M solution of sodium hydroxide in water, and an aqueous-alcoholic solution of bromphenol blue.

The reaction begins abruptly as soon as the aqueous solution is mixed with the acetone solution of *tert*-butyl chloride. As long as hydroxide is in excess, the solution (with several drops of indicator added) will remain deep blue, but at the instant the base is entirely neutralized, the indicator makes a sharp transition to yellow.

$$(CH_3)_3CCl + HOH \rightarrow (CH_3)_3COH + HCl$$

A typical experiment is indicated below in which the sodium hydroxide represents 10 mole % of the *tert*-butyl chloride and the solvent system is 70% water and 30% acetone by volume. The time for 10% reaction under these conditions is sufficiently short that student laboratory time is used efficiently allowing many variations of the experiment to be done in a 3-hr period. Because the rate of change of acidity becomes less as the reaction proceeds, it is undesirable to follow the reaction to a large percentage of completion. Under these circumstances the indicator does not change color sharply, but passes through several shades of green thus making the time measurement more difficult to reproduce.

Procedure

Pipet 3 ml of a 0.1 M solution of *tert*-butyl chloride in acetone into a 25-ml Erlenmeyer flask and place it on a piece of white paper.

Pipet 0.3 ml (1-ml pipet) of the 0.1 M NaOH solution into the other 25-ml Erlenmeyer flask followed by 6.7 ml of distilled (or deionized) water (small graduated cylinder or pipet). Add 3 drops of the bromphenol blue indicator solution.

Note the time and pour the acetone solution into the water solution quickly, swirl for a second and immediately pour the solution back into the other flask. (This procedure will insure complete mixing of the two solutions.) *Before beginning each new experiment, the two flasks should be rinsed with acetone and drained.*

The results can be tabulated in terms of the time for a particular per cent reaction or can be expressed as a standard rate constant by using equation (1).

$$kt = 2.303 \log \left(\frac{1}{1 - \%\text{Rxn.}/100}\right) \qquad (1)$$

The above expression can be easily derived from the integrated first order rate law, $\ln([\text{RCl}]_0/[\text{RCl}]) = kt$, by defining the fraction of reaction as $([\text{RCl}]_0 - [\text{RCl}])/[\text{RCl}]_0$. The derivation of equation (1) can be effectively given as an exercise to interested students who have had some physical chemistry background.

In addition it might be of interest to have several students measure the time and corresponding rate constant for a reaction carried to 20 or 30% completion in order to show that the rate constant is independent of initial hydroxide concentration.[3]

Reaction Order

The order of the reaction is most easily determined by noting the effect of a change in reactant concentration on the time necessary for any given per cent reaction, e.g., the half life or tenth life.[4]

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[1] FROST, A. A., AND PEARSON, R. G., "Kinetics and Mechanism," John Wiley and Sons, New York, 1953.

[2] STREITWIESER, A., Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, 1962.

[3] Although the effectiveness of the experiment in no way depends upon the exact reproduction of literature values, these values can be easily obtained for a variety of solvents and at various temperatures by using the tabulated data in the reference cited in footnote 2.

Use the experimental procedure described previously, but before the two solutions are mixed, add 10 ml of a 70% water-30% acetone solution to the Erlenmeyer flask which contains the aqueous sodium hydroxide. (The reaction is being carried out at twice the total dilution that was used in the previous experiment, but the relative amount of water and acetone in the solvent remains the same.)

Because the time for 10% reaction is independent of the substrate concentration, the student can readily show that the solvolysis is first order in *tert*-butyl chloride.

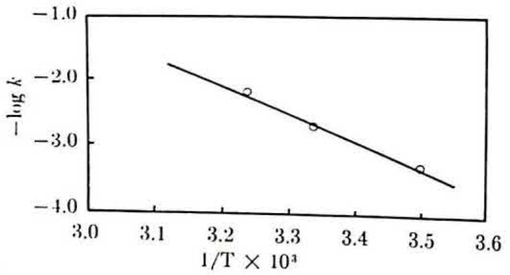

Figure 1. Student results for hydrolysis of *tert*-butyl chloride. E_a = 19.3 kcal/mole, calculated from slope.

Temperature Variation

The rate determination carried out at room temperature should be repeated at two additional temperatures to illustrate in a quantitative fashion the marked temperature dependence of the rate constant.

Prepare a water bath from a large beaker and adjust the temperature (crushed ice) to about 10° below room temperature. Before you mix the two solutions (see general procedure above), allow the temperature of the Erlenmeyer flasks to equilibrate in the water bath for about 5 min. (A piece of copper wire wound around the neck of the flasks and hooked over the edge of the beaker provides a convenient support.) Try the reaction at least twice.

Warm a large beaker of water to about 10° above room temperature and repeat the above experiment twice.

The method described here is readily adapted to very large organic laboratory sections and in spite of its simplicity, provides results of sufficient accuracy that an approximate activation energy can be obtained. (Data at room temperature is obtained from the first experimental procedure.) Figure 1 shows a student's Arrhenius plot.

Solvent Polarity

A unimolecular solvolysis reaction provides an excellent opportunity to demonstrate the importance of solvation in decreasing the energy difference between a highly polar transition state and a slightly polar ground state.[5] Various mixtures of acetone and water ranging from 80 to 60% water by volume will change the time for 10% reaction of *tert*-butyl chloride by a factor of approximately 10.

Pipet 2 ml of a 0.1 *M* acetone solution of *tert*-butyl chloride into one of the Erlenmeyer flasks and 0.2 ml of the 0.1 *M* NaOH solution plus 7.8 ml of water and three drops of bromphenol blue indicator into the other flask. (80% water-20% acetone.) Carry out the reaction as previously described and carefully record the results.

Design and carry out an experiment to measure the time for 10% reaction of *tert*-butyl chloride in a 60% water-40% acetone solvent.

Structural Variations in the Substrate

Prepare a 0.1 *M* acetone solution of isopropyl chloride or *sec*-butyl chloride and repeat the first experimental procedure. After 5 min, heat the reaction mixture on a steam bath.

The entire experiment is designed for flexibility. If time is limited, portions of the experiment can be omitted without loss of continuity. Pertinent questions and discussion material are left to the discretion of the instructor.

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[4] See Frost and Pearson (footnote 1), p. 40.

[5] See Streitwiser (footnote 2), p. 43.

Reprinted from *Chemistry*, Vol. 37, No. 2, 1964, pp. 23-27.

THIN LAYER CHROMATOGRAPHY

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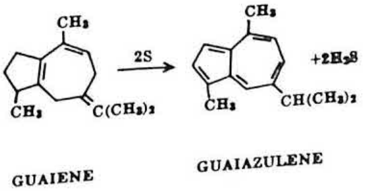
In "Chemistry in Three Dimensions" (*1*), a book intended for use in the study of organic chemistry with plastic tetrahedral models (*2*), the author recommended the experiment of isolating the red pigment lycopene from tomato paste. He now suggests that the experiment becomes more meaningful if it is part of a group program to provide pigments for an exciting introduction to thin layer chromatography. The lycopene isolable from 5 grams of tomato paste by the procedure given below amounts, at most, to 0.75 mg. of the red hydrocarbon, but this quantity suffices for numerous chromatograms. Half of the group can apply the same procedure to strained carrots and so provide a supply of β-carotene.

Guaiazulene, a hydrocarbon characterized by the rich blue color in solution or as an oil, is easily prepared by dehydrogenating guaiene with sulfur in a high-boiling water-soluble solvent, followed by steam distillation. The blue oil that distils contains colorless impurities, but these do not interfere with chromatography. Guaiazulene is the azulene chosen because guaiene is manufactured from a precursor alcohol of guaiac wood and is used in soap and cosmetic perfumes. It has excellent fixative properties as well as a pleasant soft odor. If the reaction mixture from 10 ml. of guaiene and 2.5 grams of sulfur is divided among 10 students for steam distillation, each can have the pleasure of observing droplets of blue oil condensing along with the water. Individual dehydrogenations on one tenth the scale would call for facilities for weighing which may not be available.



The Chromatographic Technique

A 1 × 3 inch microscope slide is coated on one side with a thin layer of alumina and dried. A tiny amount of a solution of the substance to be examined is spotted on the slide about 1 cm. from the end. The plate is then grasped at the other end with a forceps and lowered into a 4-ounce wide-mouthed bottle containing 4 ml. of an organic solvent. The glass stopper is put in place and the time noted (Figure 1). The solvent travels rapidly up the thin layer of alumina by capillary flow. If the substance is a pure colored compound capable of being eluted by the solvent, a spot appears, either traveling along with the solvent or at some distance behind the solvent front (leading edge of solvent). If two colored compounds are present and an appropriate solvent is selected, two spots will appear. Differences in structure or in molecular weight produce differences in the tenacity with which compounds are adsorbed on alumina and hence

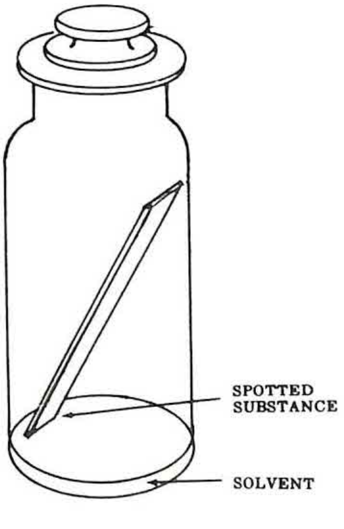


Figure 1. Thin layer chromatography assembly

their rate of flow (*Rf*) with respect to the flow of solvent. The *Rf* value of a given compound for a specific adsorbent-solvent system is given by the equation:

$$Rf = \frac{\text{Distance traveled by substance}}{\text{Distance traveled by solvent}}$$

The distance traveled by the substance is measured from a starting line to the front (top) of a spot.

Preparation of Plates. The adsorbent recommended is a preparation of alumina containing plaster of paris as a binder. [FAF alumina (Fluka alumina), Gallard-Schlesinger Chemical Mfg. Corp., 1001 Franklin Ave., Garden City, L. I., N. Y.; Aluminum Oxide, Kensington Scientific Corp., 1717 Fifth St., Berkeley 10, Calif.]

Slides should be washed clean with water and a detergent, rinsed thoroughly with water, and placed on a clean towel to dry. A dry slide should be grasped by the two sides or the two ends, or with a forceps, without touching the working surface with the fingers.

Place 2 grams of adsorbent and 10 ml. of distilled water in a 25-ml. Erlenmeyer flask; stopper the flask, and shake it to produce an even slurry. Keep the flask stoppered when not in use. Place a clean, dry slide on a block of wood or a box with the glass projecting about 1 cm. on the left-hand side (if you are right-handed) so that it can be grasped easily on the two sides. Swirl the flask to mix the contents and draw a portion of slurry into a medicine dropper. Hold the dropper vertically and, starting at the right end of the slide, apply the slurry until the entire upper surface is covered; make further applications to repair pinholes, and eliminate bubbles with the dropper. Grasp the left end of the slide with a forceps, and even the emulsion layer by tilting the slide slowly to the left to cause a flow and then to the right; tilt it again to the front and then to the rear. The coated slide is conveniently dried on a 3-inch 70-watt hot plate (Wilkens-Anderson Co., 4525 West Division St., Chicago 51, Ill.) using as supports two double pairs of 1 × 7 cm. strips of asbestos paper (or a pair of applicator sticks) resting on the edges of the hot plate. Use a forceps to transfer the wet slide to the hot plate and to remove it for cooling. Drying takes 2 to $2^1/_2$ minutes and the end point is apparent from inspection. A coated slide or plate, *when cool,* can be grasped at either the two sides or the two ends without disturbing the layer. The amount of adsorbent slurry specified suffices for the preparation of about 16 plates.

Marking and Spotting. Place a coated plate over the accompanying template (Figure 2) and draw a horizontal line between the upper arrows wide enough to bare the glass and stop the solvent. The space above this line can be used for writing in appropriate data such as plate number and starting time. At the bottom make small marks to indicate each end of the starting line for guidance in placing spots at the position shown. If you later allow the solvent to rise just to the finish line, you can place the developed plate over the template and read off *Rf* values directly.

Spotting is done with micropipets (either style shown in Figure 3) made by drawing out a 5-mm. soft glass tube. The bore should be of a size that, when the pipet is dipped deep into benzene, solvent flows in to form a tiny thread which, when the pipet is withdrawn, does not flow out to form a drop. Style *A* has an advantage in that it can be cleaned, by introducing solvent benzene with a capillary dropping tube (Arthur H. Thomas Co., 145 mm. pipet, capillary 8216-D, with 2 ml. rubber bulb 8773-C) and shaking it out. To apply a test solution, let a 2 to 3 cm. column of solution flow into the pipet. Hold this vertically over a plate; lower it until the tip just touches the adsorbent and liquid flows onto the plate; and withdraw it when the spot is about 3 mm. in diameter. Make a second spot about 4 mm. in diameter; one spot may develop more satisfactorily than the other.

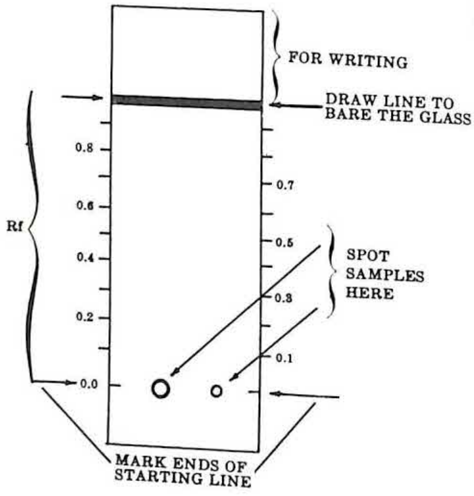


Figure 2. Template for marking coated plates

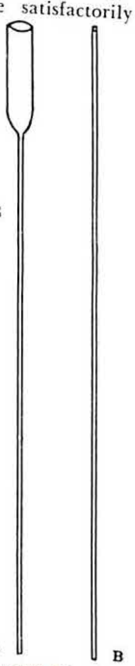


Figure 3. Micropipets

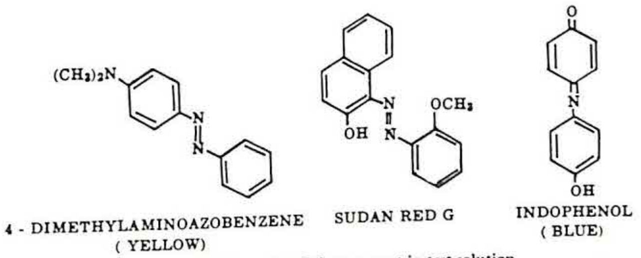


Figure 4. Formulas of dyes present in test solution

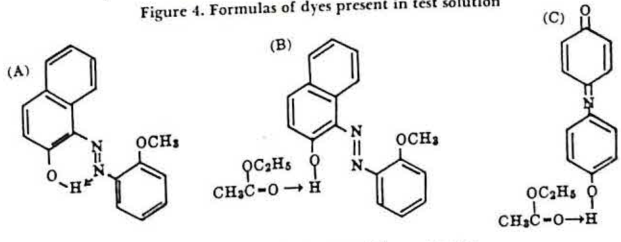


Figure 5. Interaction of solvent and dye molecules

Experiments with Dyes

A spectacular introduction to the chromatographic technique utilizes a benzene test solution (Brinkmann Instruments, Cantiague Road, Westbury, N. Y., test mixture 25 10 33) containing a yellow dye, a red dye, and a blue dye of the structures formulated (Figure 4).

In the first experiment, make two spots of the dye solution as described, and lower the plate with a forceps into a 4-ounce widemouth bottle containing 4 ml. of benzene. Noting the running time and whether or not separation is accomplished, record the *Rf* values and draw a diagram of the spots. The second experiment suggested differs only in that the solvent is a mixture of 3 ml. of benzene and 1 ml. of chloroform.

In each of these first experiments clean separation of the three dyes becomes apparent in a minute or two; it is evident that the yellow dye travels the fastest and that the red and the blue dyes follow in turn. Why? Well, the yellow dye is nonhydroxylic (contains no OH groups) and hence is more like the nonhydroxylic solvents (C_6H_6 and $C_6H_6 + CHCl_3$) than the hydroxyl-containing red and blue dyes. The red dye contains a hydroxyl group, but it probably exists in the hydrogen-bonded form *A* (Figure 5) and hence is less hydroxylic than the blue dye, which is incapable of internal hydrogen bonding. The most hydroxylic dye in this system would be eluted most slowly by the solvent.

For a surprise, run another chromatogram of the test dye solution in a bottle containing 4 ml. of a mixture of 8.5 ml. of cyclohexane (C_6H_{12}) and 1.5 ml. of ethyl acetate ($CH_3CO_2C_2H_5$). The yellow dye again leads the field, but the order of the red and the blue dyes is reversed. The probable explanation is that the carbonyl (C = O) oxygen atom of ethyl acetate forms a hydrogen bond with the hydroxyl group of the red dye stronger than that from the nearby nitrogen and the dye exists in form *B*; the blue dye forms the similar complex *C*, and since *C* is comparable to *B* but of smaller molecular size, it travels faster with the solvent than does *B*.

Two further experiments, which present problems in interpretation, include running chromatograms on the test dye solution with cyclohexane (4 ml.) and with chloroform (4 ml.) as the eluent solvents. In the first run, the mixed-colored spot does not move from the site of origin, and the result shows that none of the three dyes is soluble enough in cyclohexane to be eluted from the alumina. In the other, chloroform elutes all three components so readily that they travel nearly together along with the solvent front with poor separation.

Hydrocarbon Pigments

In addition to the blue hydrocarbon guaiazulene, other pigments to be chromatographed are lycopene (red) from the tomato and β-carotene (yellow) from the carrot. In all three hydrocarbons the color is attributed to the presence of extended conjugated systems—that is, systems with alternating double and single bonds.

These unsaturated hydrocarbons are very sensitive to photochemical air oxidation which produces colorless products, particularly when they are exposed on a thin layer of adsorbent. During the formation of a chromatogram they are protected by solvent vapor, but on removal of a plate from a chamber, a spot may disappear rapidly, and it should therefore be outlined immediately in pencil.

In accordance with the rule that like dissolves like, the hydrocarbons would be expected to be eluted by a hydrocarbon solvent such as benzene or cyclohexane. Guaiazulene, being the smallest of the three, should travel the fastest with the solvent. Those who try these experiments will find this to be true and will observe that β-carotene travels ahead of lycopene. They should run one chromatogram of the three hydrocarbons in cyclohexane and another in benzene; if the blue pigment is spotted in the center lane and if care is taken to make the spots small, it should be possible to run the three hydrocarbons together on one plate. If either solvent fails to effect separation of the red and yellow pigments, the failure should be understandable from the results of the preceding experiments on dyes. Having outlined the spots on a plate showing resolution of all three pig-

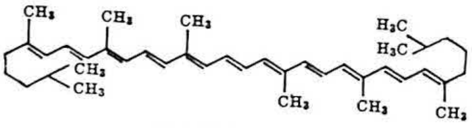


Figure 6. Lycopene

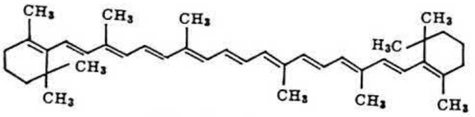


Figure 7. β-Carotene

ments, note the order in which the spots disappear on exposure to air.

The chromatographic characterization of the lycopene and β-carotene samples presents points of particular interest. The tomato is reported to contain one part of β-carotene to 10 parts of lycopene; do the experiments provide evidence for the presence or absence of β-carotene in the lycopene sample? Another problem for consideration is that of the possibility of separating a mixture of lycopene and β-carotene, say 1 gram of each. Those who have been indoctrinated in the microanalytical technique of thin layer chromatography should be able to comprehend easily the preparative technique of column chromatography. They should be advised, however, that the pigments differ markedly in solubility. For example, 7.7 mg. of lycopene dissolves in 100 g. of hexane at 0° C., compared to 109 mg. of β-carotene.

A rational procedure for separating the 1:1 mixture would be first to crystallize the material from a hydrocarbon solvent, with reasonable expectation of obtaining a crystallizate consisting of pure or almost pure lycopene. Material recovered from the mother liquor could then be adsorbed on alumina; elution of the column with hexane should yield initial fractions containing pure β-carotene.

Fluorescence

Anthracene is a colorless hydrocarbon, and when a benzene solution is applied to a thin layer of alumina and let dry, no spot is visible. However, if the plate is viewed under a source of ultraviolet (UV) light a beautifully fluorescent spot is observed. The plate should then be lowered into a chromatogram chamber containing benzene and the solvent allowed to travel for a few centimeters. The travel of the anthracene spot cannot be followed during the running of the chromatogram under UV irradiation because the glass of the bottle absorbs UV light. However, if the plate is removed from the chamber and examined under a UV lamp, a fluorescent spot that can be outlined in pencil appears.

DO NOT LOOK INTO UV LIGHT, for eye injury may result.

Next place the plate in a 4-ounce bottle containing a few crystals of iodine (USE SPATULA) and close the bottle with a glass stopper. If no change is easily apparent after a few minutes, remove the plate for closer inspection and see if the encircled spot has turned brown where iodine vapor has dissolved in the anthracene that has migrated. The technique of iodine development is the standard method for following thin layer chromatograms on organic compounds that are colorless and nonfluorescent, but some practice is required to attain proficiency in identifying the brown spots. An iodine spot once detected should be outlined in pencil at once, for the iodine soon volatilizes, and the spot disappears.

Preparation of Pigments

Guaiazulene. Place 10 ml. (9.0 grams) of guaiene (Aldrich Chemical Co., Milwaukee 10, Wisc.): 2.5 grams of sulfur; and 25 ml. of triethylene glycol dimethyl ether (Eastman Organic Chemicals' 1,2-Bis (2-methoxyethoxy) ethane; b.p. 222°; miscible with water) in a 100-ml. round-bottomed flask mounted in a clamp over a microburner (hood). Attach a reflux condenser and in the opening insert a one-hole No. 5 rubber stopper, carrying a short glass tube, along with an applicator stick between the stopper and the condenser to make a vent to the atmosphere. Connect the glass tube to the suction pump, and apply enough suction to sweep the hydrogen sulfide formed down the drain. Add a carborundum boiling stone, heat to boiling, and reflux the mixture for one hour. A blue color is soon apparent, but at the end it is masked by brown impurities. Cool the dirty mixture to room temperature and use a metal-scoop, one tablespoon measure, to divide it into 10 parts, each of which is poured into a 250-ml. distilling flask. Fill the flask half full with water, connect the flask to a condenser for downward distillation, insert a boiling stone and a cork stopper, and distill rapidly until the residual volume is reduced to about one half. Cool the condensate if it is warm, and rinse blue oil adhering to the condenser into the receiving flask with a little methanol or acetone (care, flammable). Pour the condensate into a separatory funnel, and rinse out the flask with 25 ml. of benzene (flammable). Add the benzene solution to the funnel, and shake to bring the blue azulene all into solution in the benzene. Then run out and discard the water layer. Run out the blue benzene solution into a small flask, and add a little anhydrous sodium sulfate to absorb adhering water. The benzene solution of guaiazulene is then ready for use in chromatography.

Lycopene and β-Carotene. Commercial tomato paste is a satisfactory starting material since it contains only about 74% of water and is free from the seeds and skin of fresh tomato fruit, the water content of which is close to 96%. A jar of strained carrots (baby food) serves as a convenient source of β-carotene.

A dispenser is made by connecting an 18-cm. section of 11-mm. glass tubing by means of a No. 00 rubber stopper and a short section of 5 mm. glass tubing to a 50-cm. length of $^1/_8$-inch rubber tubing. The open end is calibrated to deliver 5 grams of tomato paste and marked with a file scratch.

Thrust the dispenser into a can or jar of fruit paste and suck up paste to the scratch mark. Then wipe the tube with a facial tissue, insert it into a 25 × 150 mm. test tube, and blow out the paste onto the bottom of the receiver. Wash the dispenser tube clean with water and leave it upright to drain for the next user.

Add 10 ml. of 95% ethyl alcohol, insert a cold finger condenser (Figure 8), heat to boiling, and reflux for five minutes. Then filter the hot mixture on a small suction filter. Scrape out the tube with a spatula, let the tube drain thoroughly, and squeeze liquid out of the solid residue with a spatula. Pour the yellow filtrate into a 125-ml. Erlenmeyer flask for storage. The solid residue is now sufficiently dehydrated to be extracted with a solvent more effective for dissolving hydrocarbon pigments. Return the solid residue, with or without adhering filter paper, to the original test tube. Add 10 ml. of methylene chloride (CH_2Cl_2, b.p. 41°, sp. gr. 1.4. USE HOOD), insert the condenser, and reflux the mixture for three to four minutes. Filter the yellow extract, and add the filtrate to the storage flask. Repeat the extraction with two or three further 10-ml. portions of methylene chloride. Pour the combined extracts into a separatory funnel, add water and a little saturated sodium chloride solution (to aid in layer separation), and shake. Run the colored lower layer through a cone of anhydrous sodium sulfate into a dry 125-ml. Erlenmeyer flask and evaporate to dryness on a steam bath in the hood. The residue is the crude carotenoid pigment, lycopene or β-carotene.

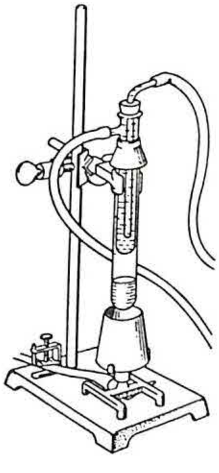


Figure 8. Reflux assembly with cold finger condenser

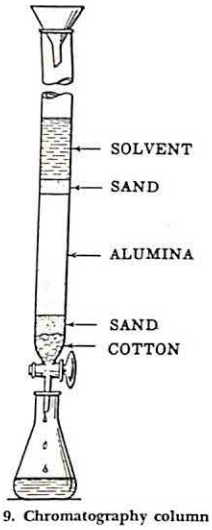


Figure 9. Chromatography column

Purification is accomplished by chromatography on acid-washed alumina (Merck) in a column packed as shown in Figure 9. Close the stopper of an ungreased 50-ml. buret and fill it to the 35-ml. mark with 30 to 60° petroleum ether. With a wooden dowel, push a small plug of cotton through the solvent to the bottom of the buret, dust in through a funnel enough sand (dry) to form a 1-cm. layer over the cotton, and level the surface by tapping. Unclamp the buret and with the right hand grasp both the top of the buret and the funnel, so that the whole assembly can be shaken to dislodge alumina that may stick to the walls. With the left hand slowly pour in 12 grams of alumina from a test tube. When the fine powder has settled, add a little sand to form a protective layer at the top. Open the stopcock, let the solvent level fall until it is just above the upper layer of sand, and then stop the flow.

Dissolve the crude carotenoid pigment in a few milliliters of benzene, and with a capillary dropping tube transfer the solution to the column. Put a 50-ml. Erlenmeyer flask in place as receiver, open the stockcock, and elute the column with 30 to 60° petroleum ether—that is, pour in solvent to fill the tube, and add additional portions as required. Discard initial colorless fractions and collect all yellow or orange eluates together in a 50-ml. Erlenmeyer. Place a drop of solution on a microscope slide, and evaporate the rest to dryness. Examination of the material on the slide under a microscope after the solvent has evaporated may reveal crystallinity. Then put a drop of concentrated sulfuric acid beside the sample, and mix with a stirring rod. Compare the color of your test with that of a test on the other carotenoid.

Finally, dissolve the sample in the least amount of methylene chloride, hold the Erlenmeyer in a slanting position for drainage into a small area, and transfer the solution with a capillary dropping tube to a 10 × 75 ml. test tube. Add a tiny carborundum boiling stone, hold the test tube over a hot plate in a slanting position, and evaporate to dryness. Cork and label the test tube, and keep it in a dark place. When a solution is required for thin-layer chromatography, add about 0.5 ml. of methylene chloride and shake. The sample may not all dissolve because of partial air oxidation to insoluble material, but there should be enough colored supernatant liquid for numerous experiments. Keep the solution out of light, and when no more is required evaporate off the solvent for safer storage.

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LOUIS F. FIESER is Sheldon Emery professor of organic chemistry at Harvard University. He did his undergraduate work at Williams College, where he was linesman on the unbeaten football team of 1919. His Ph.D. is from Harvard. A distinguished teacher, he has for some time engaged in an annual laboratory competition with his assistants and students synthesizing a series of crystalline naphthalene derivatives.

Professor Fieser was a member of the Surgeon General's Advisory Committee on Smoking and Health. He has published more than 300 research papers and written a number of books on organic chemistry, several of them jointly with his wife, Mary Fieser.

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Hamlet the basset hound probably owes his keen sense of smell to a gas chromatographic process

GAS CHROMATOGRAPHY SNOOPER PAR EXCELLENCE

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Applied Science Laboratories, Inc., State College, Pa.

As far as the general public is concerned, gas chromatography itself has received little attention but the information it is uncovering by snooping into areas such as food and water supplies is. Products previously considered pure have been found to contain many other components, and frequently even brand names and sources can be identified.

In terms of pesticides, publication of the book, "Silent Spring," triggered the controversy, but gas chromatography has kept it alive. Minute quantities in the range of 10^{-12} gram can be detected, and because of this, insecticides on vegetables can be identified, even after the vegetables have been washed and placed on market shelves. This accomplishment has led to two other problems: fixing maximum allowable content of insecticides in food products and establishing their effect on the human metabolism.

In 1906 Michael Tswett, a Russian botanist, percolated a solution of chlorophyll through a column packed with pulverized calcium carbonate and found that fractions of chlorophyll separated into colored bands. He called the process chromatography.

However, the process observed by Tswett (liquid-solid chromatography) still today has definite disadvantages—when most solutions are percolated through packed columns, separation into colored bands does not occur, and no good method has been developed to identify fractions as they emerge from the column. Therefore, the liquid is generally collected in small portions, each of which must be analyzed separately.

Later another process was developed. In 1941, two British chemists, A. J. P. Martin and R. L. M. Synge, published a paper (5) on liquid-liquid partition chromatography using a liquid (mobile phase) percolated through a tube packed with solid particles which had been coated with another liquid (immobile phase) immiscible with the first. In one small paragraph they suggested that a gas might replace the liquid mobile phase and a nonvolatile liquid coated on the inert solid particles could be the immobile phase. Thus, a mixture of two or more compounds vaporized into a gas could be separated according to their volatilities and solubilities in the liquid which had been coated on the particles. However, because of World War II, this suggestion was laid aside. Then during the fifties, the technique was developed rapidly and became known as vapor-liquid partition chromatography, then vapor-liquid or gas-liquid chromatography, and finally gas chromatography. Technically the term can refer to gas-solid chromatography, but more often it applies to the gas-liquid type as used in this article. In this process, components of mixtures can be detected automatically as they emerge from the column.

In the brief span of 15 years gas chromatography has resulted in a major breakthrough in separation and analysis of complex mixtures of gases, liquids, and solids because it can analyze minute quantities of material (micrograms to milligrams). However, samples must be vaporizable at the temperature of operation, and for this reason gas chromatography has found its greatest use in organic chemistry. Recently though it has been used to a limited extent for inorganic compounds where higher temperatures are required.

Basic Principles of Chromatography

All chromatographic processes, of which gas chromatography is but one, have two basic parts: a mobile and an immobile phase. The immobile phase may be either liquid or solid. If solid, it is usually in the form of a powder packed into a tube, and if liquid, it is usually coated as a thin film on particle surfaces of a solid packed into a tube. The mobile phase, either a gas or liquid, moves through the tube, percolating through the granular immobile phase. The sample to be analyzed (a mixture of two or more components) is injected into the column, and as it is swept forward by the mobile phase, its components are

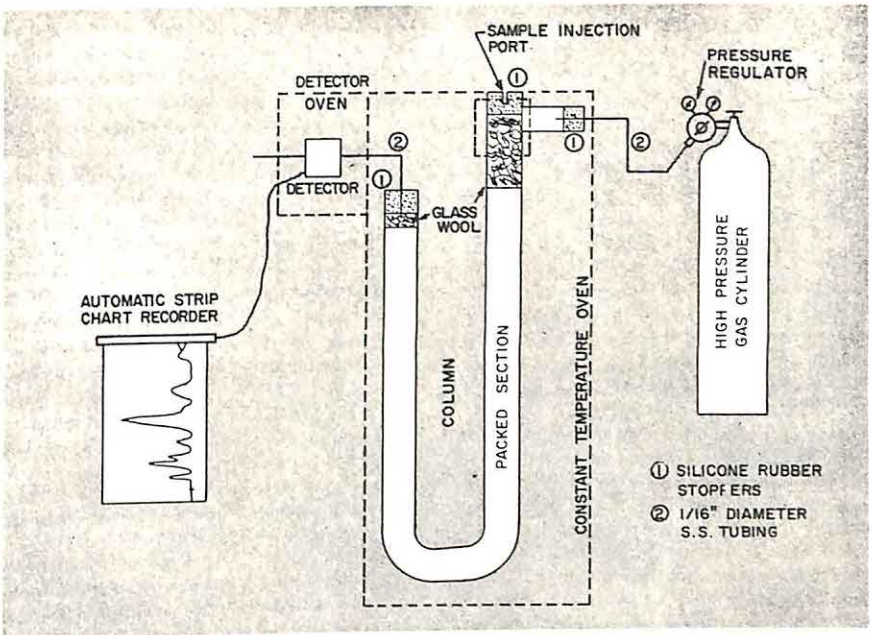

SAMPLE INJECTION PORT
①
PRESSURE REGULATOR
DETECTOR OVEN
②
①
②
①
DETECTOR
GLASS WOOL
AUTOMATIC STRIP CHART RECORDER
COLUMN
PACKED SECTION
CONSTANT TEMPERATURE OVEN
HIGH PRESSURE GAS CYLINDER
① SILICONE RUBBER STOPF ERS
② 1/16" DIAMETER S.S. TUBING

Figure 1. A gas chromatograph consists of three main parts: sample injection section, separation column, and a detector which monitors the gas mixture leaving the column. The detector indicates relative amounts of components and time they leave the column. S. S. = stainless steel

adsorbed onto the surface of the immobile phase (if solid) or dissolved in the immobile phase (if liquid).

As pure mobile phase passes into the column behind the sample, components of the sample desorb back into it. This adsorption-desorption process continues through the column. Since molecules in the sample spend some of their time in the immobile phase they move through the column more slowly than those in the mobile phase. Also because each component moves at a different rate, depending on its attraction for the immobile phase, the components separate as they pass through the column and emerge at the other end at different times.

A Gas Chromatograph

Figure 1 is a schematic drawing of a gas chromatograph used in our laboratories. Figure 2 is a photograph showing at the right the column and detector ovens, which are home-made. The unit on the left, consisting of the recorder and electronics for the detector, is part of a Barber-Colman Model 20 chromatograph.

The mobile phase, usually called the carrier gas, commonly is helium, argon, or nitrogen contained in a high pressure cylinder. Gas pressure at the column inlet is usually maintained at 10 to 25 pounds per square inch, but the column outlet and detector are usually at atmospheric pressure. Gas flow rate is determined by the column inlet pressure.

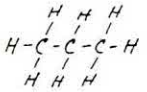
The sample, either a liquid or a solid dissolved in a volatile liquid, is injected with a small syringe through the silicone stopper which is self-sealing. The sample is deposited in the glass wool which is maintained at a temperature of 50° to 100° C. above that of the column. This causes rapid vaporization of the sample, which is then carried into the packed section of the column. As it travels along this path, the components, moving at different speeds, separate and emerge from the column at different times. The gas stream then passes through the detector which senses changes in some physical property of the stream and converts the change into an electrical signal which is automatically recorded as a peak on a strip chart recorder. The result, a continuous record of detector signals *vs.* time, is called a chromatogram.

Columns and Packing. Gas chromatographic columns, made usually from glass or metal tubes, can be straight, U-shaped, or coiled. Diameters range from $^1/_8$ to $^1/_4$ inch and lengths from 1 to 20 feet. The packing consists of small particles of an inert solid (support), commonly diatomaceous earths, consisting mostly of silicon dioxide coated with a liquid which is usually

Figure 2. Photograph of the chromatograph

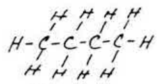
nonvolatile at room temperature. The liquid, ranging from 1 to 20% of the packing weight, is then mixed with a volatile solvent, slurried with the support, and spread on a tray to allow the solvent to evaporate. The nonvolatile liquid remains coated on the support. Such a coated support appears dry and is free-flowing. Frequently coated and uncoated solvents differ very little in appearance.

The chromatographic columns normally are contained in constant temperature ovens operated at different temperatures, depending on volatility of the sample being analyzed. Low volatility requires higher temperatures than high volatility. Temperatures can vary from below room temperature to 300° C. and in special cases up to 1000° C., but use of higher temperatures is limited by the type of materials from which chromatographs can be made and availability of liquid phases which can withstand high temperatures. No liquid is completely nonvolatile and volatility increases with temperature. Therefore in actual practice liquids continually bleed off a column and gradually change its characteristics so that ultimately the column must be replaced. However, at lower temperatures, bleed rates are small and columns can be used for several months to a year. At high temperatures bleed rate increases and columns deteriorate rapidly. Other factors which may limit higher operating temperatures are decomposition of the liquid phase and either chemical reaction between the sample and liquid phase or catalytic decomposition of the sample by the liquid phase.

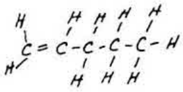


PROPANE

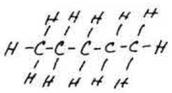
Because of volatility limitations, most liquid phases used above 200° C. are polymers such as silicones, polyesters, and polyglycols, many of which are solid at room temperature but liquefy at operating temperatures.



BUTANE



PENTENE-1



PENTANE

The degree to which sample components are separated depends on their solubility in the immobile phase deposited as a thin film on the support. All components dissolve to some extent, but the least soluble, swept by the carrier gas, emerges from the column first. If the proper immobile phase is used, differences in solubilities are sufficient for complete separation prior to emergence from the column.

Some stationary phases separate components according to boiling points, but others will retain components having certain functional groups. For example a paraffin-type stationary phase will separate propane, butane, pentene-1, and pentane in that order (according to boiling points). Polyethylene glycol, however, will separate in the order of propane, butane, pentane, and pentene-1. In many cases, components having essentially the same boiling points can be separated by the proper choice of columns.

Hundreds of different materials are used as the liquid phase. "Rules of thumb" are available for selecting these materials for a specific analysis but the novice should first read some basic texts on gas chromatography and then consult some abstracts to determine whether or not a mixture similar to his has already been analyzed.

Column length and diameter, as well as nature and amount of liquid phase used, also influence the degree of separation obtained. The retention time of a peak is defined as the time elapsed between injection of the sample and emergence of the maximum concentration point from the column outlet. The degree of separation between two peaks depends on the ratio of their retention times and on the ratio of the width of each peak to its retention time, W/t_R. The ratio W/t_R is influenced also by column length and diameter—increasing with decreasing diameter and decreasing with increasing length.

Various liquid phase loadings (amounts of liquid phase relative to support) are used to control retention times, which in turn determine the time required for analysis. As loading increases, retention time also increases. Sometimes, very low loadings are required; for example, steroid loadings are 1 to 3% of packing weight.

Column and Detector Ovens. These ovens are essentially thermostated boxes usually made of metal and well insulated. In most column ovens air is circulated with a fan or blower. The detector oven is separate and maintained at a temperature higher than that of the column oven to ensure that no condensation of sample components occurs.

Vaporization Chamber. In Figure 1 the vaporization chamber is part of the column, but in other instruments it is sometimes a small heated metal block placed ahead of the column. The design of the chamber is critical for many applications. The sample must be vaporized rapidly to avoid fractionation which causes some of the less volatile components to remain in the chamber and eventually carbonize. This causes error in the analysis and sometimes irreversible adsorption of polar samples introduced later.

Detector. The thermal conductivity detector, commonly used to monitor the gas stream emerging from the column, consists of a matched pair of heated resistance wires mounted in two separate compartments. Gas from the column flows through one compartment, and carrier gas which has bypassed the injection port and column flows through the other. In both compartments the gas flow cools the wires and thus

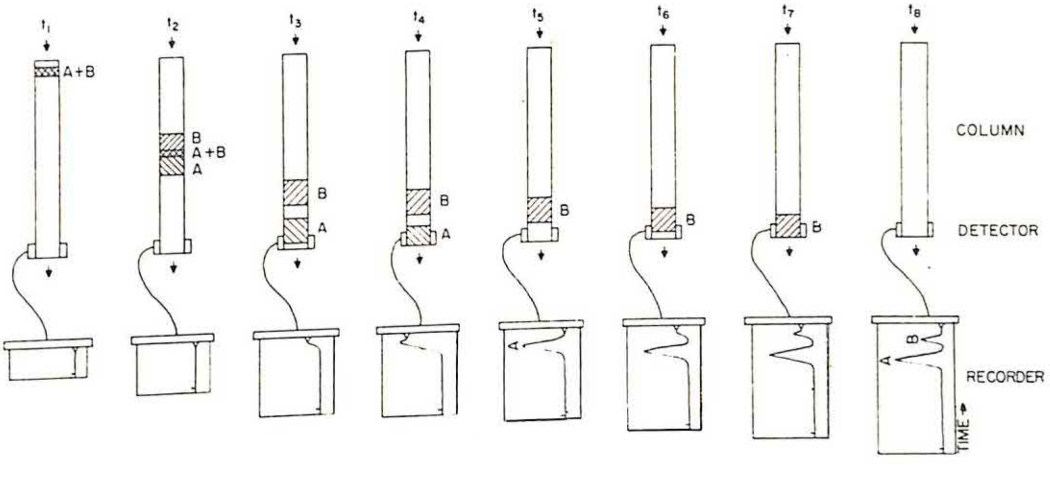


Figure 3. Development of the chromatogram. Paper in the automatic strip recorder moves continuously under a pen which is driven electrically by signals from the detector. Direction of pen is perpendicular to movement of the paper. t = Time

- t_1. Sample containing components *A* and *B*
- t_2. *A* and *B* are starting to separate but neither has reached the detector
- t_3. *A* and *B* have separated and part of *A* has reached the detector
- t_4. Point containing maximum concentration of *A* has passed detector. Pen reverses direction
- t_5. *A* has passed the detector and pen returns to zero after tracing a peak for *A*
- t_6. *B* reaches detector
- t_7. Point containing maximum concentration of *B* has passed detector. Pen reverses direction
- t_8. *B* has passed detector and pen after tracing a peak for *B* returns to zero

changes their resistance. When no samples flow through the column, resistance change of both wires is the same; however when a sample is introduced and its components flow through one compartment the wire there is cooled more than the other and its resistance increases. The difference in resistance is then indicated on a strip chart recorder as shown in Figure 3.

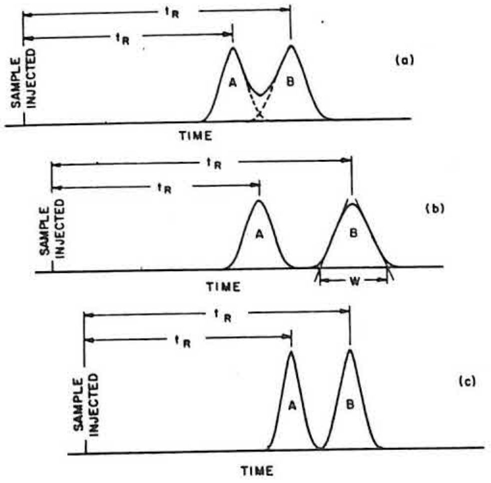
Other types of detectors commonly used involve ionization of the sample components in a high potential electrical field and amplification and measurement of the resulting ionization current. Detectors of this type are highly sensitive.

Qualitative and Quantitative Analysis

The qualitative aspects of chromatography are important—unknown components can be tentatively identified by comparison with known standards and two unknown mixtures can be compared, even though no reference standards are available. Given a certain chromatographic column operated under specific conditions, a certain mixture of components will give the same chromatogram tracing each time it is analyzed. Hence if two mixtures give different chromatograms the conclusion is reasonable that the mixtures differ in composition even though their components are unknown (Figure 4). On the other hand, if the tracings are identical it cannot be assumed that composition of mixture is identical. One may contain two components which have not been separated and the other may contain only one of these components. Qualitative analysis is possible because, given constant operating conditions, a particular compound will be retained in a given column for the same length of time regardless of how many times the analysis is performed.

Figure 4 (Below). Separation of components *A* and *B*

- *a.* Incomplete separation
- *b.* W/t_R for each peak is the same as in *a*, but separation is complete because the ratio of retention times for the two peaks has been increased
- *c.* Relative retention times are the same as in *b* but separation is complete because the ratio of width to retention time has been decreased



The retention time depends on type and amount of immobile phase coated on the solid support; column temperature, length, and diameter; and flow rate of the carrier gas. Some components can be identified by comparing retention time with that of a known standard. But many compounds have the same retention time, and therefore identification by this means must be considered tentative unless additional information is available. Frequently other techniques of identification are used, such as infrared analysis.

In a chromatogram for multicomponent mixtures, the relative area under each peak depends on percentage of that component in the original sample. In many cases the relative area is equivalent to the percentage composition but for this to be true the equipment must be in proper adjustment and the components must be similar in chemical nature. If two components are present in equal quantities but differ chemically they may appear to be present in a markedly different ratio. Therefore to obtain an accurate qualitative analysis, identity of the components must be established. When this has been done, relative areas under the peaks can be converted to percentages by using correction factors determined from analysis of a reference standard. Also a known amount of a standard can be added to the sample before analysis, but the standard should be merely similar chemically to the components and not identical.

Temperature-Programmed Procedure

Gas chromatographic analyses are carried out either at constant temperature (isothermally) or by temperature programming which is useful for complex mixtures containing several components having a wide range of volatilities. If the analysis is run isothermally at a low temperature, too much time is required for the less volatile components to emerge from the column. If the temperature is too high, the more volatile components emerge too fast and bunch up, resulting in poor separation.

With temperature programming, the analysis is started at low temperature which is then continually raised. Thus the more volatile components emerge slowly enough to be separated and the less volatile fast enough to be practical.

Applications

The controversy aroused partially by publication of "Silent Spring" has contributed to the rapid development of techniques for analyzing pesticides. The ultrasensitive electron capture detector, capable of detecting quantities in the range of 10^{-12} gram, can identify insecticides used on vegetables even after the produce has been washed and placed on supermarket shelves. Bache and others (*1*) have determined that tomatoes which received four pounds of 2,5-dichlorobenzoic acid (amiben) per acre contained about 0.03 part per million of this insecticide on harvesting. The Government's problem is in fixing the maximum allowable content of these insecticides in food products. Now that they can be detected in small quantities, their effect on human metabolism in these concentrations must be established.

It has been said that "gas chromatography has made the chemist honest." The technique has shown that many compounds previously considered pure actually contain many other components. Where products normally contain a variety of components, the brand or source frequently can be identified. The analysis of food products by gas chromatography has developed rapidly because it is a convenient and rapid method for determining quality. Adulteration of cooking oils can be detected more readily. Many margarines, cooking oils, and other products are promoted as beneficial because of their high "polyunsaturated" content. The term polyunsaturated in this case refers to the polyunsaturated fatty acids, mainly linoleic acid which has two double bonds within its 18-carbon-atom chain length. Linoleic acid is a major constituent of cottonseed oil. Olive oil consists primarily of oleic acid which has only one double bond within its 18-carbon chain. Stearic acid, which has the same chain length but is completely saturated, is the major component of lard.

Although the chromatograms for a type of oil may vary somewhat depending upon the season, the country in which the plant was grown, the species, and other factors, the patterns are generally quite similar. Consequently, it is relatively simple to determine whether a sample is cottonseed, olive (Figure 5), or peanut oil. Sometimes oils used to prepare a blend can be identified but this is difficult and requires more experience. One of the problems confronting the food industry is adulteration of lower priced oils to give them the appearance of higher grade products. Development of chromatographic techniques makes such adulteration more difficult.

In some instances the chromatograph column, instead of being filled with a coated support, may consist of a long capillary tube which has the stationary phase coated directly onto the inside wall. These columns in many cases are capable of producing significantly better separations than are the conventional packed columns.

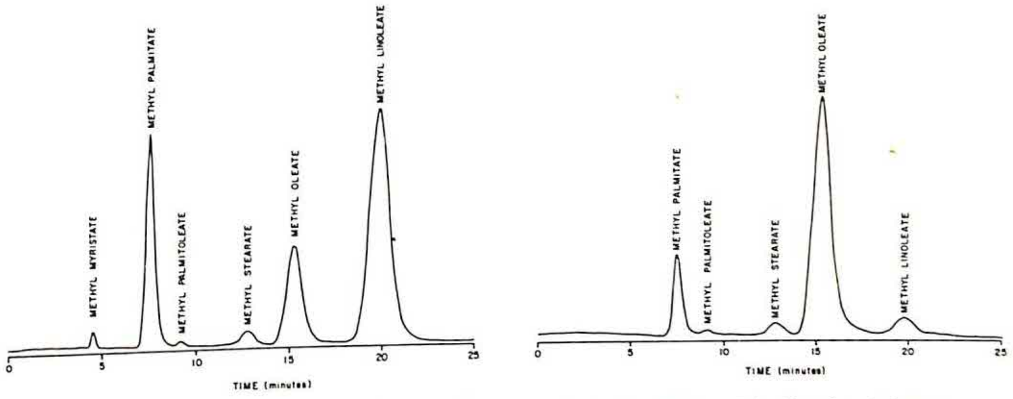


Figure 5. Chromatograms for edible oils. Left, Wesson oil (cottonseed oil) methyl esters. Right, olive oil methyl esters

Capillary columns have been very useful for analyzing very complex mixtures—for example, to determine changes occurring during storage (*3*), an analysis of orange oil indicated at least 72 components were present; only 23 were tentatively identified. After the oil had been heated for 20 hours, several new peaks appeared, and the proportion of many other components had changed. Some of these have not yet been identified, and consequently the relationship to flavor change must yet be determined.

Preparative gas chromatography is one specialized area which has contributed immensely to our knowledge of the composition of many natural and synthetic products. Frequently conventional separation techniques such as distillation, extraction, and crystallization are not efficient enough to separate completely all of the components in a complex mixture. Gas chromatographic analysis, based upon the separation of the individual components, is conducive to the preparation of the individual components in a highly purified state.

However, an efficient collecting system is needed at the end of the column because amounts collected are relatively small. Usually the amount of sample to be purified is considerably larger than can be handled by a single injection into column. One method of overcoming this is to use larger columns, although this sacrifices separation efficiency. Columns up to one inch in diameter are often used and there are a few references to larger sizes. A more common technique for purification of large quantities of material is the use of a chromatograph equipped with an automatic sample injection and collection device. Here, a sample can be injected repeatedly on a cyclic basis and the components collected in separate containers. Many such units are commercially available.

Preparative gas chromatography may be used to obtain highly purified compounds for use as reference standards, or for subsequent chemical synthesis. One of the more common uses, however, is to isolate unknown components in sufficient quantities so that other methods of analysis can be used for identification purposes. This technique has been used, for example, to identify some of the components in cigarette smoke, smog, strawberry oil, liquors, and fuel oils.

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A New Freshman Chemistry Laboratory Program

Recent improvements in the teaching of high school chemistry and the advent of general chemistry texts with a change in emphasis plus the availability of undergraduate equipment grants from the NSF have brought changes in many first year college chemistry courses.

The purpose of this article is to describe a pilot chemistry program which was initiated at Rensselaer Polytechnic Institute three years ago.[1] The content of the course was directed toward the understanding of fundamental principles with the assumption that all of the students in the program had taken a year of high school chemistry. The textbook used in the program was "Principles of Chemistry" by Hiller and Herber. Ten percent of the freshman class (80 students) took the course.

In the second year of the program, about one third of the freshman took the pilot course (about 300 students). Students selected were a typical cross section of the freshman class with no particular orientation toward chemistry. In the present academic year the entire freshman class is taking this course (approximately 800 students).

The program consists of two lectures, one recitation period, and one three-hour laboratory period each week. The lectures are given by eight professors, with each professor lecturing in those areas of his specific research interest. All the lectures are attended by the entire staff involved in the course. In addition, recitation sections are handled in groups of about 40 students by the lecturers plus additional professors from the department. Only two well-proved graduate students have recitation sections; the other sections have full-time staff at their helm.

The idea of having different professors lecture in the course has some interesting aspects. To cite one advantage, the students look forward to viewing a new face and new idiosyncrasies. Secondly, the staff enjoys seeing how a professor handles a particular topic. It is safe to state that the professors probably enjoy their colleague's lectures more than the students do. They are certainly more appreciative of the effort involved.

Sometime early in this transition period at RPI, it was realized that important changes had to be made in the laboratory to make this new level of material more pertinent. What follows is an outline and brief description of the current freshman laboratory program at RPI, which we feel is a logical compliment to the new outlooks in introductory college chemistry.

The Laboratory Program

The laboratory is headed by one professor in charge who devotes practically full time to this program. Each of the eight laboratory sessions is under a staff member's supervision and the laboratory assistants are full-time graduate students majoring in chemistry.

In the first semester, each student has his own qualitative analysis desk for the laboratory period; however, the same desk is used by seven other students during other laboratory periods. The same system is applied to the quantitative analysis experiments. As long as an ample supply of glassware (especially test tubes) is in each desk, there is little temptation for students to disturb corked and labeled test tubes. To the amazement of the teaching staff, there were very few instances of students not finding left-over materials.

The remaining experiments in the first and second semester are scheduled on a staggered system. Eight students (4 groups of 2 each) perform an individual experiment each week. Thus, each experiment scheduled for a particular semester is performed every week of the semester by rotating small groups of students. In order to have each experiment performed simultaneously each laboratory period, it has been found necessary to have four instruments in operation each period with the exception that only two Infracord instruments were available. With four instruments, the shutdown of one instrument for minor repairs is not serious. During the past year there were no major repairs needed for any of the instruments in spite of their extensive use.

Description of Experiments

All the freshman chemistry students have one three-hour laboratory period a week. In a fifteen-week semester there are an introductory laboratory session, twelve laboratory periods, and two weeks for testing, makeups, and repeat experiments. A report for each experiment is filled out in duplicate by the students. One copy of the report sheet is turned in to the instructor a week after the experiment is performed, and the second copy is kept by the students. Each report sheet has space for experimental data and contains a number of questions pertinent to the particular experiment. At the outset of the first semester all the students work on qualitative analysis. The principal reason for doing this is to make the students work independently in the laboratory. The pace is a bit slow at the start, but students acquire basic techniques fairly rapidly, and most of them finish the required amount of work in the seven weeks allotted to qualitative analysis. For the very fast students, general unknowns and anion analyses can be performed in the time remaining.

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[1] This program was developed by Professors L. G. Bassett and H. M. Clark with the cooperation of the entire Chemistry Department, and in particular Professor H. M. Faigenbaum.

Two weeks are allotted for learning basic quantitative techniques in the gravimetric analysis of a soluble chloride salt. The accuracy generally required in a sophomore quantitative analysis course is expected for this experiment.

Since organic chemistry and structure are taught in lecture during the first semester, the last three experiments in the first semester are designed to complement these subjects. The preparation of *n*-butyl bromide acquaints the students with the techniques of refluxing, distillation, solvent extraction, and purification. The entire synthesis takes about 2 hours; the remaining hour is spent calculating yields, and checking the purity of the product by means of a Perkin-Elmer Model 154 Gas Chromatograph. A laboratory instructor must spend 15 min showing the students the basics of the instrument, and must be available while the students are operating the gas chromatographs.

Infrared spectra are obtained for salicylic acid and the synthesized aspirin on a Perkin-Elmer Model 137 Infrared Spectrophotometer. The spectra are compared, and a very simple functional group analysis is performed. The instrument is very simple to operate and the necessary infrared techniques can be demonstrated in about 10 min. The laboratory instructor is available for consultation and extra help during these final stages.

A three-hour laboratory session devoted entirely to the construction of molecular models, with time out to review, compare, and draw structures is very helpful to the students. Fisher-Taylor-Hirschfelder models are used in this experiment, and the students construct the following molecules: aliphatics such as propane and butane, substituted aliphatics and an illustration of isomerism, benzene, and various substituted benzene derivatives, illustrations of optical activity with asymmetric carbon atoms, and inorganic hexacoordinated complexes.

During the second semester twelve experiments are carried out. It is unusual that experiments of the caliber performed in the second semester are staged so early in a students college career. No attempt was made to dream up a set of "oddball" experiments, but an effort was made to select experiments that are meaningful in relation to the lecture material with the use of equipment that the students will see again for many years to come.

Phase relationships are studied in the experiments entitled Chemical Microscopy and Crystal Growth and a Two Component Phase Diagram. Simple microscopes are used in the crystal growth experiment, and the habits of inorganic materials such as sodium chloride and potassium dichromate are observed. Students are then required to comment on the simple kinetic factors leading to the structures they observe under the microscope. In the two-component phase diagram experiment, the students determine the entire liquidus-solidus curve of a simple binary system like naphthalene-*p*-dichlorobenzene. Boiling water and cold tap water are the only temperature baths required in this experiment.

Experiments are carried out in volumetric analysis, column adsorption chromatography, and freezing point depression. Since these experiments are fairly standard, they need no additional comments. The experiment involving ionic solution kinetics enables the students to obtain and analyze kinetic data for a simple clock reaction like the persulfate-iodide ion system. The next experiment deals with the inorganic synthesis of two complexes of Co(III). These complexes are carbonatotetramminecobalt(III) nitrate and chloropentaamminecobalt(III) chloride. Good laboratory technique is necessary in this experiment, and by this stage most of the students can perform the experiment successfully.

The determination of at least one important constant of chemical interest is desirable in a freshman chemistry laboratory. Avogadro's number is determined coulometrically by the electrolysis of water. Two second semester experiments deal with equilibrium in solution. The first experiment is the determination of the equilibrium constant of an indicator, such as bromcresol green. The equilibrium constant is obtained colorimetrically with a Bausch and Lomb Spectronic 20. The second experiment is the potentiometric determination of Fe(II) ions by titration with Ce(IV) solutions. A Leeds and Northrup student potentiometer is used in this portion of the experiment. The *p*H titrations employing simple Photovolt *p*H meters form the basis of the second portion of this experiment.

An experiment in gas chromatography deals with the qualitative and quantitative analysis of multicomponent mixtures. An aromatic mixture of benzene, toluene, and the xylenes is analyzed, as well as an aliphatic mixture of isomers of hexane, heptane, and octane.

A thermodynamics experiment is also included in the second semester laboratory program. The heat of precipitation of aluminum hydroxide is measured using Dewar flasks as calorimeters.

The last experiment is in the field of radiochemistry and deals with two applications of this area of work. These two applications are the determination of the half life of ^{144}Pr and a distribution equilibrium of ^{210}Bi between water and chloroform containing 8-hydroxyquinoline. The nuclides chosen are of such activity that no radiation hazard involving special laboratory arrangements is involved. All chemical manipulations in this experiment are drastically simplified and carefully worked out in order to minimize any possible spillage.

Conclusion

The consensus of the staff and teaching assistants involved in supervising the laboratories is that the experiments are quite effective and a decided complement to the lecture material. The students generally enjoy doing the experiments and are appreciative and respectful of the expensive instruments used. It is anticipated that more experiments will be added to the list already in use. However, only experiments of the same general level will be added. The authors would be happy to send further details of the laboratory program to interested parties.

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MODELLING OF CHEMICAL STRUCTURES WITH EXPANDED POLYSTYRENE SPHERES

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The modelling of chemical structures with expanded polystyrene spheres has been a practice in the U.S.A. for some years, and Sanderson[1] has devised a teaching method in which his electronegativity scale is reflected in his models.

Expanded polystyrene spheres are now manufactured in Britain[2] for teaching purposes. These spheres are made from Bextrene-X polystyrene beads, to which is added a propelling agent that inflates the material when it is heated. Dow polystyrene, at present available only in the U.S.A.,[3] produces a lighter sphere with a rougher surface. Though aesthetically pleasing and easy to cut, the lighter spheres have less mechanical strength and are not suitable for some of the techniques described in this article. In addition they soften excessively on glueing and thus sometimes lose shape.

The purpose of this article is to introduce teachers to the theory and practice of the use of polystyrene spheres for modelling. The structures described are not highly accurate scale models, but they will help considerably to give students an introduction to shape in depth and states of aggregation.

In general the following broad classification of chemical structures holds :

1. *Ionic crystals*—assemblages of positive and negative ions (typified by sodium chloride).
2. *Molecular crystals*—discrete covalent units, low freezing and boiling points (exemplified by sulphur).
3. *Macromolecular structures*—*e.g.* ice, diamond.
4. *Layer structures*—*e.g.* graphite.
5. *Close-packed spheres*—as in metals.

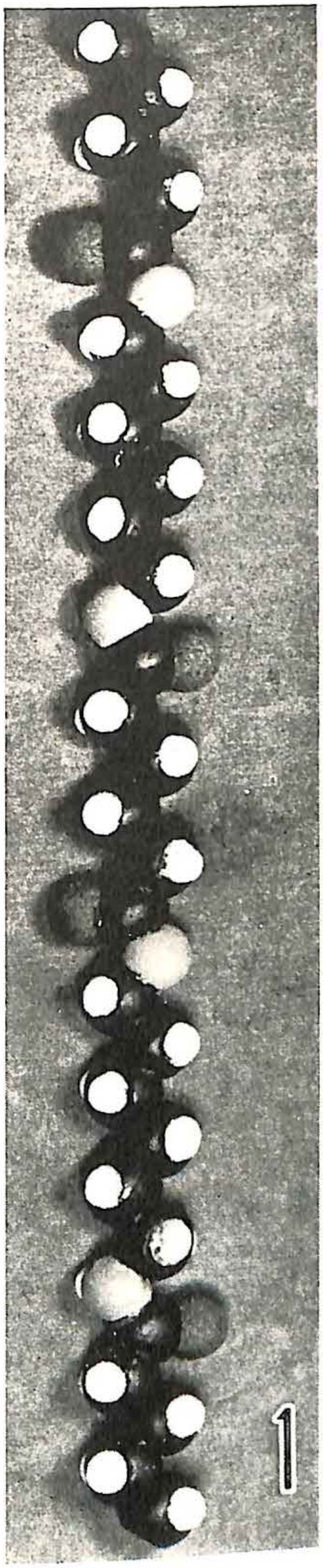
UNI-UNIVALENT IONIC STRUCTURES

Inter-nuclear distances have been calculated, mainly from X-ray measurements on crystalline solids. Similarly, data for ionic radii are readily available. These measurements are precise. Some useful values are given below.

TABLE I

IONIC RADII (Å)

Cations		Anions	
Na^+	0·95	Cl^-	1·81
K^+	1·33	Br^-	1·95
Cs^+	1·69	I^-	2·16



Model 1. Nylon 66. *Colours:* Black, White, Grey, Blue

These ions are assumed to be spherically symmetrical. Since the largest sphere available in economic quantity is of 2 in. diameter, an economic scale would be $\frac{1}{2}$ in. = 1 Å. To choose a larger scale would make chloride ions rather expensive, and as they are frequently used in modelling their cost determines the scale to be used.

In constructing ionic models it is more important to get the radius ratio (0·95/1·81 for sodium chloride) nearly correct than to match exactly the ionic radius of each ion on the scale $\frac{1}{2}$ in. = 1Å. For this reason a 1-in. sphere will be suitable for Na^+ and a 2-in. sphere for Cl^-, *i.e.* ratio about 1 : 2.

To assemble a model of the sodium chloride crystal it will be found satisfactory to join 1-in. and 2-in. spheres alternately in rows after colouring and glueing at the approximate points of contact (Fig. 1).

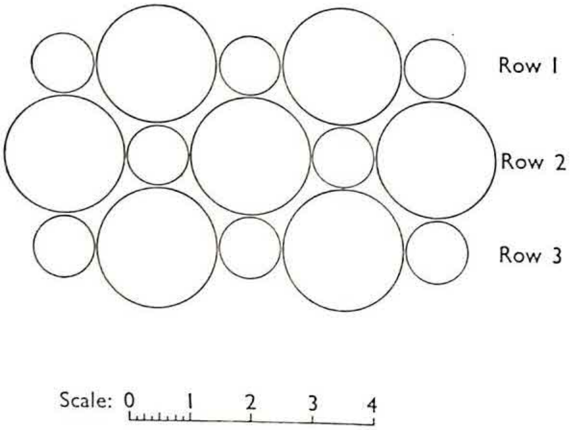


Fig. 1

While the glue is still tacky it is possible to press the rows together into the sodium chloride structure. There is sufficient 'give' in the spheres and tacky glue to adjust minor imperfections in positioning in the original rows when the structure is being finally assembled and pressed into shape.

The so-called body-centred structure of caesium chloride can be modelled from a $1\frac{3}{4}$-in. sphere for Cs^+ and a 2-in. sphere for Cl^-. Again assembly by eye is satisfactory, packing eight chloride ions round a central caesium ion with the aid of glue after colouring. It will be found that after some 50 ions have been packed minor imperfections are smoothed out, as the structure is pressed into shape while the glue is still tacky.

It has not been found necessary to drill or punch the spheres to assemble these simple 6-to-1 or 8-to-1 structures. However a template for this purpose is described later if mechanical assistance is required. Dow polystyrene spheres were found to be particularly good for these models because their low mechanical strength aids alignment by pressing, but perfectly good results are obtained with the harder Elford spheres.

MOLECULAR CRYSTALS

In molecular crystals the atoms are linked by covalent bonds into molecules but only weak van der Waals attractions or hydrogen bonds hold the molecules together in the crystal. In solid iodine, for example, two different internuclear distances are noted (Fig. 2), one corresponding to the covalently linked iodine atoms giving the so-called covalent radius (r_c), and one corresponding to the distance between unbonded atoms, the van der Waals radius (r_v).

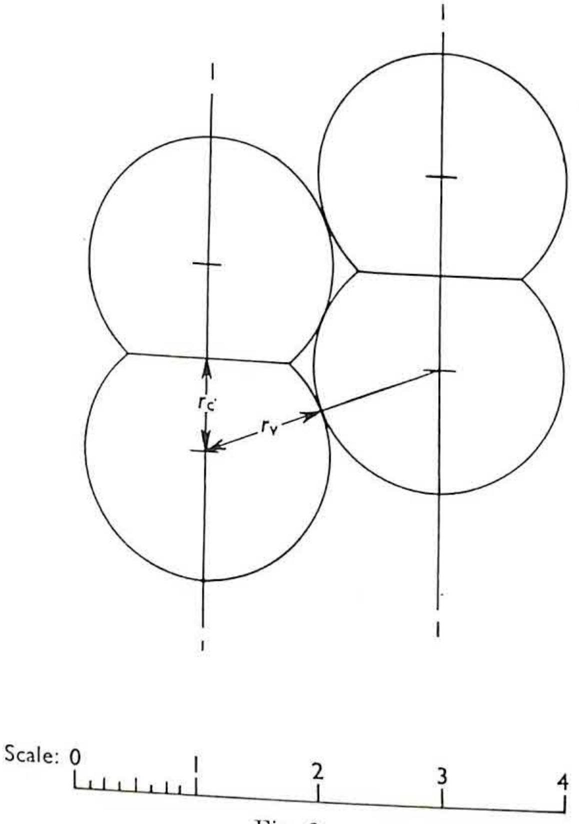


Fig. 2

For space-filling models, choose a sphere of suitable diameter to represent the van der Waals radius, r_V, and cut off a portion corresponding to the approximate covalent radius, r_c. In this way states of aggregation may be represented by packing molecules in close contact in accordance with known crystallographic data.

Tables of approximate van der Waals and covalent radii are given below for those units most frequently needed in schools. The covalent radii are taken for single bonds, but slight shortening occurs for multiple bonds. It is debatable if this shortening can be illustrated accurately with these models. If in any one model this feature requires emphasis it is suggested that the shortening be exaggerated.

TABLE II

Atom	Approx. van der Waals radius (Å)	Approx. covalent radius (Å)	Diameter of nearest suitable sphere (in.)
C	1·7	0·77	$1\frac{3}{4}$
N	1·5	0·7	$1\frac{1}{2}$
O	1·4	0·6	$1\frac{1}{2}$
S	1·85	1·0	$1\frac{3}{4}$
P	1·9	1·1	2
Si	2·0	1·2	2
Cl	1·8	1·0	$1\frac{3}{4}$
Br	1·9	1·1	2
I	2·1	1·3	2
H	1·0	0·3	1

Many molecular crystals are organic in nature, and in choosing a suitable and economic scale the price of carbon atoms becomes a governing factor. The above values fit well the previously used scale of $\frac{1}{2}$ in. = 1 Å.

Model 2. Protein α-Helix (after Pauling)
Colours: Black, White, Grey, Blue, Red

If close representation to actual size is required spheres can be reduced in size by some 10–20 per cent, depending upon their density, by rolling under pressure, *e.g.* under a sheet of thick glass. However, this process is tedious and need only be used if it becomes essential for one or two simple molecules to be modelled extremely accurately.

To fabricate organic structures it is essential to be able to cut tetrahedral carbon atoms from $1\frac{3}{4}$-in. spheres in quantity. For this purpose some form of mechanical aid is essential, and working drawings are shown (Fig. 3) for a jig which has proved very successful.

JIG FOR CUTTING TETRAHEDRA

The jig, made in hardwood by a member of our staff, is designed to present spheres at the correct angle for cutting off the faces of a regular tetrahedron with an adjustable depth of cut. The depth of cut is controlled by the thickness of packing (P)—thin plywood or cardboard is suitable. The depth of cut should normally represent about 0·8 Å (average value of r_V–r_c, Table II) for a single bond. On the present scale this is about $\frac{3}{8}$ in. and for this reason the cutting guide of the jig is about $\frac{3}{8}$ in. from the inner face of the end of the jig. With smaller spheres a $\frac{3}{8}$-in. cut, if the central atom is multi-bonded, removes so much of the sphere that its 'teaching value' is destroyed by being virtually hidden. It is therefore preferable to sacrifice accuracy, making a somewhat shallower cut (after adjusting the packing) so that the central atom is still just visible. In such a case it is advisable to make and present both models with appropriate comment.

To use the jig a sphere is passed down the sloping guide and pressed against the packing, and the first face is cut with a tenon saw. It is then turned so that the cut face is flat against one side of the V groove of the sloping guide, passed down the guide to the packing and the second face cut. The third and fourth faces are cut with the two previously cut faces in contact with the sides of the V groove.

Simpler mechanical aids can be devised for

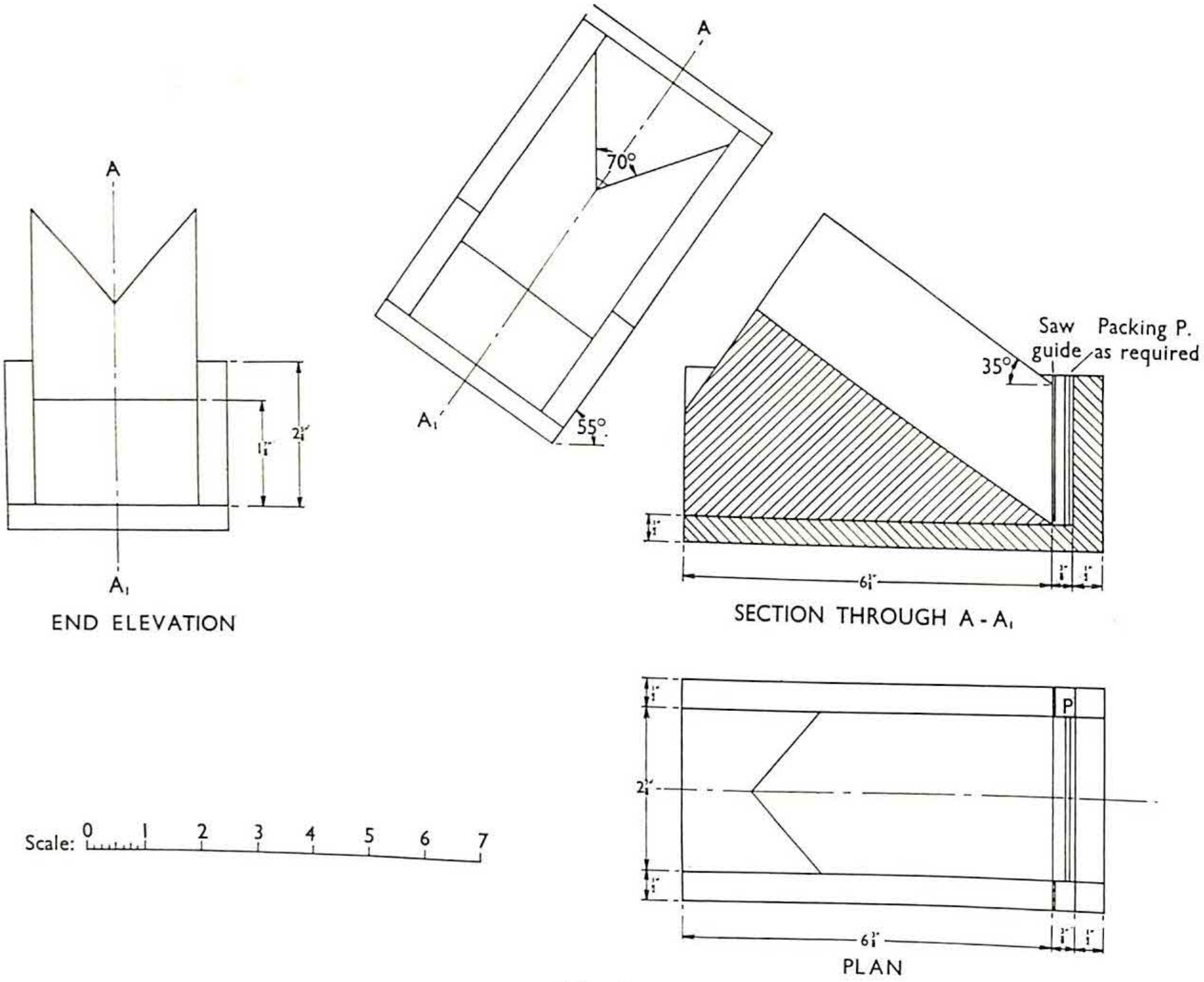


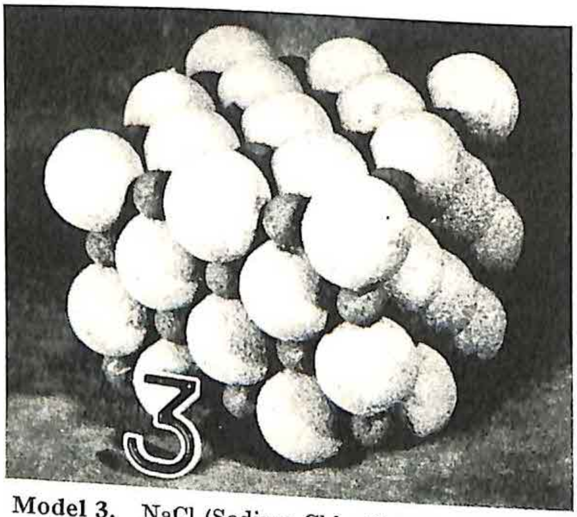
Fig. 3

cutting planar atoms, of bond-angle 120°, but satisfactory results are obtained by cutting by eye over an equilateral triangle drawn on paper. This method is recommended for uncommon bond-angles.

It has been found possible to use this 109½° (tetrahedral angle) jig for structures in which the angle is not quite 109½°, because spheres soften somewhat under the influence of glue and on pressing into shape tend to adjust to the more correct bond angle. Any angle of 109 ± 5° can be so accommodated.

PUNCHING SPHERES FOR BALL-AND-STICK MODELS

If it is desired to construct 'ball-and-stick' models, mechanical assistance is needed to



Model 3. NaCl (Sodium Chloride)
Colours: Red (Small Spheres),
Green (Large Spheres)

punch or drill spheres for 4–1, 6–1 and 8–1 structures. A template described by Mr H. Bassow[4] of Fieldston School, New York, has proved invaluable for this purpose and can be used as an aid if needed in modelling CsCl and NaCl.

To make the template *two* pieces of packing-case cardboard (corrugated sandwich type) are marked out as shown in Fig. 4. The radial lines are very heavily grooved, and the central circle, corresponding to a tight fit of the sphere to be punched, is cut out. Separate templates are needed for each size of sphere. The two pieces are glued together, so that the grooved radial lines (and central cut-outs) correspond and form guide lines for punches. The punches are best made by pointing suitable lengths of $\frac{1}{16}$-in. welding rod on a grindstone.

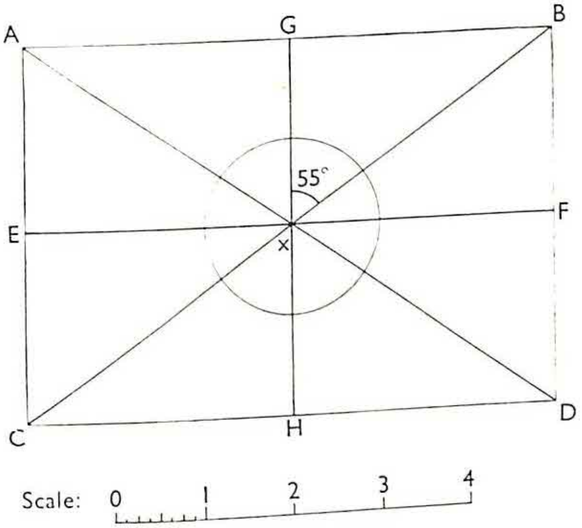
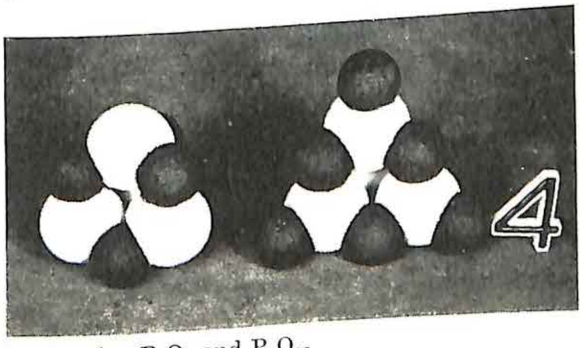


Fig. 4



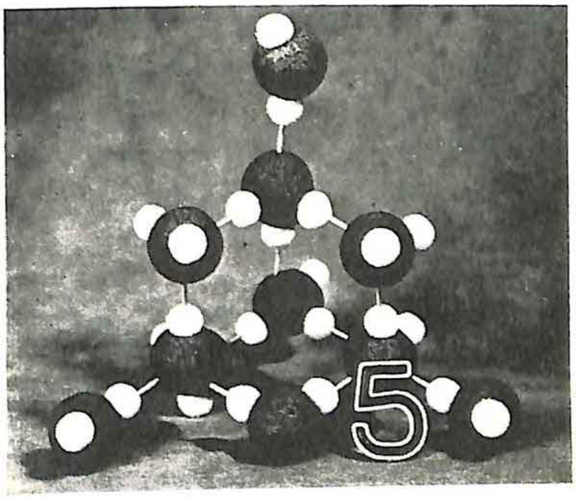
Model 4. P_4O_6 and P_4O_{10}
Colours: Light Yellow (Large Spheres),
Blue (Small Spheres)

For tetrahedral holes a sphere is located centrally in the template, punched along AX and BX, rotated through 90° about GH and punched along CX and DX.

For 8–1 structures the sphere is placed centrally and punched along AX, BX, CX and DX; it is then rotated through 90° about GH and the procedure repeated.

For 6–1 structures the sphere is punched along EX, FX, GX and HX, rotated about GH through 90°, and repunched along EX and FX.

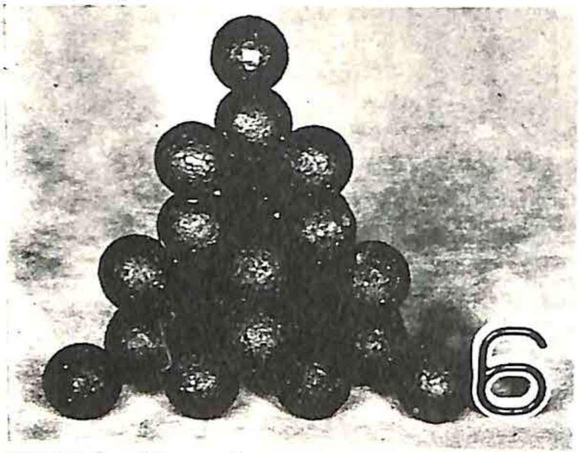
Cocktail sticks inserted into the punch holes can be used successfully for these ball-and-stick models.



Model 5. Ice I
Colours: Blue (Large Spheres), White

MACROMOLECULAR STRUCTURES

It has not been found possible to get a good model by assembling by eye. For diamond (Model 6) it is necessary for the spheres to be punched or cut tetrahedrally to obtain an accurate start. To model ice I, spheres representing oxygen atoms are punched tetrahedrally (Model 5); two of the punched positions are then cut and glued to hydrogen to make water molecules; and the other two punch-marks are linked by cocktail sticks to hydrogen of neighbouring water molecules to simulate hydrogen bonds. About $\frac{1}{2}$ in. of the cocktail stick is visible, the rest is embedded with glue in the spheres. This is the method adopted by the author to represent hydrogen bonds in general.



Model 6. Diamond
Colour: Black

CLOSE PACKING OF SPHERES

Cubic and hexagonal close packing can be demonstrated by glueing layers of spheres together as shown in Fig. 5. It is found that two alternative positions are possible for a third layer placed above the two below—either

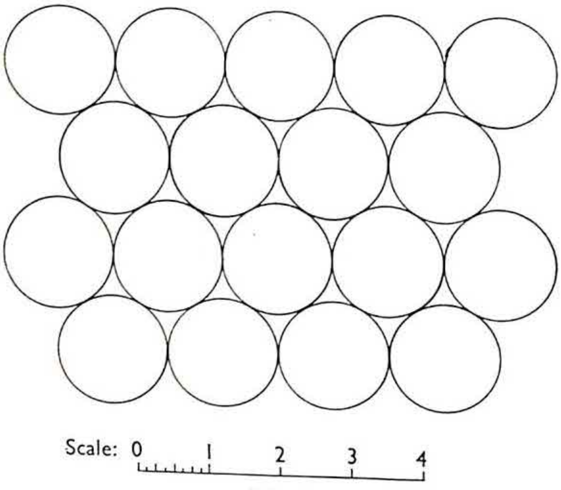


Fig. 5

(*a*) directly over first-layer spheres (hexagonal close packing)

or (*b*) over spaces between first-layer spheres (cubic close packing).

LAYER STRUCTURES

A graphite model is made from $1\frac{3}{4}$-in. spheres cut for 120° bond-angles. It should be noted that two alternative ways of placing a third layer over two lower layers are possible, demonstrating the existence of α- and β-graphite. It is necessary to use at least 24 carbon atoms per layer to obtain a model of sufficient size to make this clear.

Molybdenum disulphide, the automobile lubricant additive, has a layer structure, which can be modelled from data provided by Wells.[5]

GEOMETRICAL ISOMERS

Spheres, instead of being glued, can be bored with a hot metal rod. Holes are made centrally and perpendicularly through bonding faces towards the cêntre, and the spheres are then threaded on elastic under slight tension. (Dow polystyrene spheres will not stand up to this treatment.) If cyclohexane is modelled by this method the 'boat' and 'chair' forms are easily interconverted to supplement the permanent models of each form.

COMPLEX STRUCTURES

By assembling spheres on elastic after cutting to the correct bond angles, the suggested α-helix of proteins (Model 2) can be successfully modelled. About 36 skeletal carbon and nitrogen atoms are assembled in correct order on elastic. On tightening the elastic, and with slight shaking, the skeletal atoms tend to coil in a helix. Slight adjustment is required so that the hydrogen-bonded groups move into the correct relative positions. After adding carbonyl oxygen, H's and red spheres to represent amino acid residues the structure is finally hydrogen-bonded with cocktail sticks and glued up.

Nylon 66 (Model 1) can be modelled without elastic as it is more regular and comparatively 'straight.'

GLUEING OF SPHERES

A cheap and satisfactory adhesive is made by dissolving scrap polystyrene in benzene to form a saturated solution. Evostik is satisfactory but tends to soften the spheres; Bostik has less softening effect but dries more slowly.

COLOURING THE SPHERES

Water-based paints (emulsion paints) have been found to be highly satisfactory for colouring spheres, and a complete range of colours is available commercially. In the interests of economy attempts have been made to colour spheres by dyeing, following instructions and using materials kindly provided by the Dyestuffs Division of I.C.I. Ltd, but with disappointing results from a range of dyes in aqueous suspension. Solvent penetration of the spheres appears negligible and the dyes were not retained on the smooth surface. Better results were obtained with American Dow polystyrene spheres, the rough surface of these permitting penetration of the dyestuff.

The scheme of colours recommended by the author has been adopted in order that the student can readily identify the various atoms in a structure. It is, of course, made clear that we cannot say that atoms themselves are coloured but the colour used is the familiar colour or property of that element in some familiar or known state of aggregation.

Various colour schemes are listed below for guidance.

TABLE III

COLOUR SCHEMES FOR MOLECULAR MODELS

Atom	Author	Courtaulds	CHEM Study
H	white	cream	white
C	black	black	black
O	blue	red	red
N	grey	blue	blue
Cl	green	green	green
Metal	red or orange	silver-grey	aluminium paint
F	light green	light green	light green
Br	red-brown	blue-green	brown
I	violet	dark green	violet
P	yellow-white	purple	maroon
S	yellow-green	yellow	yellow

SUGGESTED STRUCTURES FOR MODELLING

1. *Ionic:* NaCl and CsCl.
2. *Layer:* MoS_2 (see Wells[5]), graphite, CdI_2.
3. *Macromolecular:* ZnS; diamond; ice I; linked SiO_4 tetrahedra (silicates).
4. *Fibrous:* nylon 66; protein chain and α-helix; atactic and isotactic polyisopropylene.
5. *Molecular structures:* cyclohexane (boat–chair); maleic–fumaric acid; hexamethylene tetramine; azobenzene (*cis-trans*); *o*-nitrophenol.
   Simpler organic molecules to demonstrate isomerism, asymmetry etc. (here the field is wide).
6. *Simple inorganic structures:* PCl_5; phosphorus oxyacids; P_4, P_4O_6 and P_4O_{10} (Model 4); S_8, and zig-zag S puckered chains; simple anions (CO_3^{2-}, NO_3^-, SO_3^{2-}, SO_4^{2-}, PO_4^{3-} etc.); and hydrated cations, *e.g.* $Al(H_2O)_6^{3+}$; H_2O_2 and O_3; halogen molecules to illustrate relative sizes; chlorine oxyacids; chlorides of second-period elements and/or third-period elements.

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Section 10 Programmed learning in chemistry

This paper by F.D. Gunstone and R.B. Moyes sets out the principles involved in preparing programmes and illustrates them with a programme for a topic in organic chemistry. There is a very useful bibliography.

The editor hopes to include a much larger section on this important topic in the next edition of "New Trends" and he would be grateful if material for possible inclusion could be sent to the Division of Science Teaching at Unesco.

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PROGRAMMED LEARNING IN CHEMISTRY

I—FIRST PRINCIPLES

By F. D. GUNSTONE, D.SC., F.R.I.C. *and* R. B. MOYES, B.SC., A.R.I.C.*

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During recent years interest in programmed learning has spread through the whole of the educational system and in this part of the article we explain and illustrate the principles involved. The technique has been used independently in all the university chemistry departments in Scotland. Part II gives an account of its experimental trial in Queen's College, Dundee.

Programmed learning is considered to be a more effective way of learning than the conventional procedures used by students in lecture rooms, libraries and studies. Because very little material has yet been published in the required form, interested teachers frequently prepare their own programmes, but to do this they need to understand the underlying principles. Two main types of programmes will be discussed: the so-called 'linear', or Skinnerian programmes, and 'branched' programmes.

LINEAR OR SKINNERIAN PROGRAMMES

Linear programmes are based on three main principles first elaborated by Professor B. F. Skinner:

(i) information to be imparted is broken down into a large number of small logical steps which are presented to the learner in sequence; each unit of presentations is called a frame;

(ii) the student makes an overt response to the material presented;

(iii) correct responses are rewarded (reinforced) immediately: the satisfaction of getting the correct answer is considered to be a sufficient reward for a student.

It is an essential part of the linear programme that students should make the correct response to the question(s) presented in each frame, and programme writers usually aim at an error rate not exceeding 5 per cent. If the error rate rises very much above this value at any point then the programme is at fault, and the writer should revise his material until the error rate is reduced to normal. Despite this, a case can be made for stiff linear programmes with slightly higher error rates for the highly motivated and highly selected groups of students to be found in centres of higher education.

A low error rate is achieved by careful attention to the following points:

(i) new material is presented in logical fashion;

(ii) each frame is carefully constructed so that there is no ambiguity in either the explanatory material or the question;

(iii) the step-size must be kept small, *i.e.* new ideas are introduced only at an appropriate rate and are linked, whenever possible, with previous knowledge;

(iv) a check is made that each item of new information is fully understood before proceeding to the next;

(v) the programme is continually revised in the light of students' responses;

(vi) cues or prompts are incorporated into the questions to assist the student. As the programme develops, however, these are gradually removed (faded) until the student is making the correct response without their assistance.

High error rates most often arise because the step-size is too large, or there is ambiguity in a frame, or the programme writer has assumed too much previous knowledge on the part of the student. As it is difficult to discover that a programme is too easy, it is useful to have a first draft that gives a high error rate and to reduce it in subsequent revisions.

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Although linear programmes can be presented on a simple machine, this is not necessary, and they are used mostly in book form or on sheets of paper. It is important that the student, having made his response to a question, should know immediately whether he is right or wrong, and this can be achieved by placing the answers immediately below each frame, which is covered until the response has been made. Once the student realizes that he is not being tested for examination purposes, cheating is not a serious problem. It is rather more important to be sure that there is no cheating when a programme is being tested.

Most of the chemistry programmes available, whether published or privately circulated, are of the linear type. When writing a programme for the first time most teachers have found it helpful to begin with a small, coherent and not too complex topic. The final arbiters of the value of a programme are the students for whom it is written.

BRANCHED PROGRAMMES

Branched programmes are less common than the linear but are claimed by some to be more effective. Material is again presented in logical fashion in frames which normally contain a question and multiple-choice answer. The student constructs his response and selects one of the answers. If he chooses correctly, the reasons for the correct answer will be explained—in case the right answer was obtained for the wrong reasons—and he then continues with the main programme. If the student selects a wrong answer the error is explained, and he is returned to the main programme by a direct or indirect route. A possible scheme is illustrated in Fig. 1.

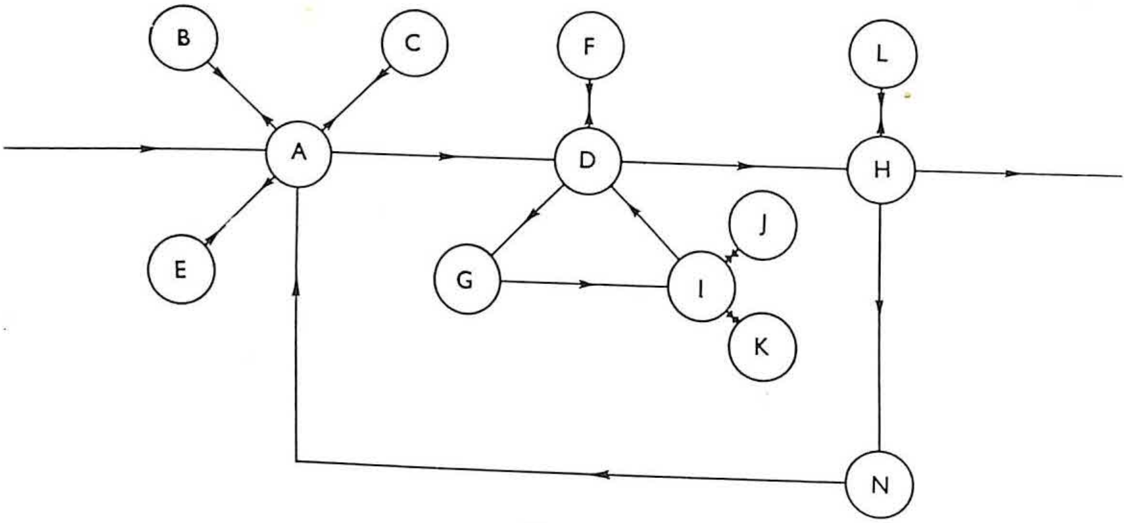

Fig. 1

In frame A the reader chooses one of four possible answers. The correct answer leads to frame D; incorrect answers lead to frames B, C and E, where the error is explained, and the student then returns to frame A to try the question again. Frame D contains a question with three possible answers. The correct answer leads to frame H and incorrect answers to F and G. In frame F the error is explained before the student is returned to frame D. In frame G the error is explained and the reader is directed to frame I where a new question is asked. The correct answer to this question then leads back to frame D, the incorrect answers lead to frames J and K. In frame H the correct answer leads to frame M (not shown) on the main programme; a minor error leads to frame L, and a more serious error to frame N. Students arriving here are considered not to have understood the material in previous frames and are directed back to frame A to work through this section of the programme again. Such schemes are capable of wide variation.

The answer serves a different purpose in the two types of programme. In a linear programme it is primarily for reinforcement; in a branching programme it controls the route through the programme. In a branching programme there is greater emphasis on correction, and error rates of up to 15 per cent are permitted. The step-size can therefore be larger and this makes the programme less tedious, particularly for the brighter student. The main disadvantage of branched programmes is that they are less convenient in book form and are best presented on expensive teaching machines.

ADVANTAGES OF PROGRAMMED LEARNING

Several benefits have been claimed for this technique by those who have devised programmes and used them with groups of students.

(i) Programme writing helps the teacher to clarify his own ideas. Whilst this is true of any teaching operation faithfully done, it is particularly true of programme writing with its insistent demand for logical development and clear presentation.

(ii) By examination of students' answers to a programme the writer quickly discovers those parts of the programme which are inadequate and what areas of the subject present students with greatest difficulty, and he has to find ways of circumventing these.

(iii) A student works through a programme at his own rate. It is found that slow students may take twice as long as their faster colleagues to complete a programme. A well-written programme can be used without outside help and so the student can choose his own times of working.

(iv) The mode of simple logical presentation and of question and answer with low error rate is of particular value for below-average students who, perhaps for the first time, get a clear understanding of the subject material and gain confidence from repeatedly getting the right answers. Such students then derive greater benefit from their normal diet of lectures and tutorials and from textbooks.

(v) Though programmes take time to prepare they save time thereafter, since one demonstrator or supervisor can help a larger number of students without any loss of efficiency. Alternatively, students can work through a programme without supervision.

Programmes written so far are crude attempts to develop this technique. There is much to be learned about the best way to write, to present and to use linear programmes, and the possibilities of branching programmes in this field of study are almost completely unexplored. But enough is known, in the opinion of some, to consider programme-learning as a useful and efficient procedure which merits further investigation and wider use in sixth forms, technical colleges and universities.

In the bibliography there is a selected list of programmes which have been prepared in various chemistry departments and circulated privately. These programmes have been well received by students who have frequently asked for further programmes on other topics, and although there has been no adequate test of the effectiveness of the programmes used, subjective expressions, based partly on the marking of degree examination scripts, are favourable. Reactions from teaching colleagues are more varied: some approve, but not always with enthusiasm; others think the technique unnecessary and harmful.

SPECIMEN EXCERPT

An excerpt from a programme on 'Ethyl Acetoacetate and Related β-Keto Esters,' designed for second-year students,* is given below. This section of the programme is followed by others on the Claisen ester condensation, the hydrolysis of β-keto esters, ethyl acetoacetate as a ketone, ethyl acetoacetate as an enol, reactions of the activated CH_2 group, and a summary. Students take

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* It must be remembered that Honours Courses in Chemistry in Scottish Universities are four years in length.

2–4 hr to complete the programme. It is regretted that most of frame 3 has had to be omitted in the interests of brevity.

When using such a programme the answers to each frame, given between the broken and the full line, are covered until the frame has been read and the answer written down on a separate sheet of paper.

PART I. THE PREPARATION OF ETHYL ACETOACETATE

1. The compound of structure $CH_3\cdot CO\cdot CH_2\cdot CO_2Et$ has the systematic name **ethyl 3-oxobutanoate** but has long been known as **ethyl acetoacetate** or as **acetoacetic ester**. It is important in the study of organic chemistry for the following reasons:

   (i) It is prepared by an important condensation reaction of wide application.

   (ii) It furnishes a simple example of the phenomenon called **tautomerism**.

   (iii) It is an important intermediate in the synthesis of many other compounds.

   Ethyl acetoacetate is a β-keto ester. Examine the formula given below and notice which carbon atoms are labelled α and β and γ.

$$\overset{\gamma}{C}H_3\cdot \overset{\beta}{C}O\cdot \overset{\alpha}{C}H_2\cdot CO_2Et$$

   Write the structural formulae of the α-, β- and γ- oxo esters based on ethyl butanoate.

   $CH_3\cdot CH_2\cdot CO\cdot CO_2Et$ (α), $CH_3\cdot CO\cdot CH_2\cdot CO_2Et$ (β), $OHC\cdot CH_2\cdot CH_2\cdot CO_2Et$ (γ)

2. Indicate whether the following structures represent α-, β- or γ- oxo esters.

$CH_3\cdot CO\cdot CH_2\cdot CO_2Me$	(*a*)	$Et\cdot CO\cdot CHMe\cdot CO_2Et$	(*b*)
$Pr\cdot CO\cdot [CH_2]_2\cdot CO_2Et$	(*c*)	$Ph\cdot CO\cdot CO_2Pr$	(*d*)
$Ph\cdot CO\cdot CH_2\cdot CO_2Me$	(*e*)	$Ph\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2Me$	(*f*)

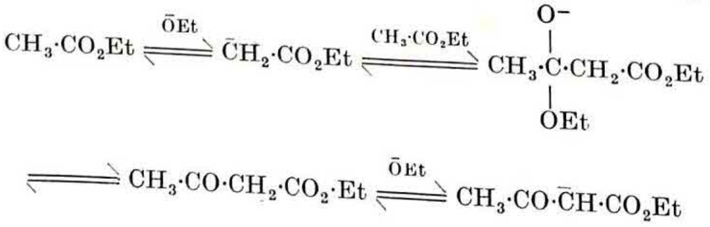
   (*a*) β, (*b*) β, (*c*) γ, (*d*) α, (*e*) β, (*f*) γ.

3. Ethyl acetoacetate is prepared by treating ethyl acetate, which usually contains necessary traces of ethanol, with sodium. The overall reaction is:

$$CH_3\cdot CO_2Et + CH_3\cdot CO_2Et \xrightarrow{Na} CH_3\cdot CO\cdot CH_2\cdot CO_2Et$$

   [The remainder of this longer-than-usual frame is an explanation of the mechanism of this reaction and is not reproduced here. *Many of the subsequent frames refer back to this material.* The frame ends in the following way.]

   Putting these steps together we get the following (note that all steps are reversible):



$$CH_3\cdot CO_2Et \overset{\bar{O}Et}{\rightleftharpoons} \bar{C}H_2\cdot CO_2Et \overset{CH_3\cdot CO_2Et}{\rightleftharpoons} CH_3\cdot \overset{O^-}{\underset{OEt}{C}}\cdot CH_2\cdot CO_2Et$$

$$\rightleftharpoons CH_3\cdot CO\cdot CH_2\cdot CO_2\cdot Et \overset{\bar{O}Et}{\rightleftharpoons} CH_3\cdot CO\cdot \bar{C}H\cdot CO_2Et$$

Continue with frame 4

4. To prepare ethyl acetoacetate, the ester ....and the metal .... are required.

ethyl acetate sodium

5. Another necessary reactant, present in the ester in sufficient quantity to start the reaction, and produced as the reaction proceeds, is ....

ethanol

6. Complete the simplified equation for the overall reaction:

$$CH_3{\cdot}CO_2Et + CH_3{\cdot}CO_2Et \xrightarrow{Na} EtOH + \text{..............}$$

$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$

7. The catalyst in this reaction is the basic .... ion.

ethoxide ($\bar{O}Et$)

8. It is produced by the action of .... on .... initially present in the ester.

sodium ethanol

9. Indicate the mechanism of this reaction by formulating each stage (take care to distinguish between reversible and non-reversible steps):

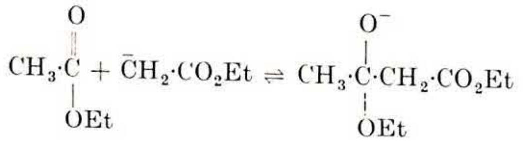
(i) Production of catalyst by reaction of sodium and ethanol.

$$2Na + 2EtOH \longrightarrow 2Na^+ + 2\bar{O}Et + H_2$$

10. (ii) Formation of an anion (carbanion) by interaction of ethyl acetate with the basic catalyst.

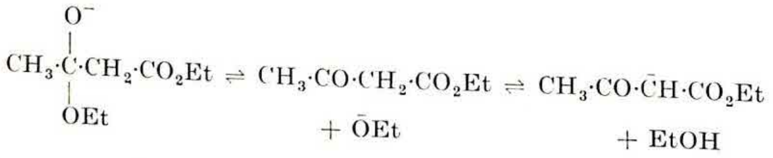
$$\bar{O}Et + CH_3\cdot CO_2Et \rightleftharpoons EtOH + \bar{C}H_2\cdot CO_2Et$$

11. (iii) Reaction of this carbanion with a molecule of ethyl acetate (this step involves addition of the carbanion to the electron-deficient carbon in the ester).



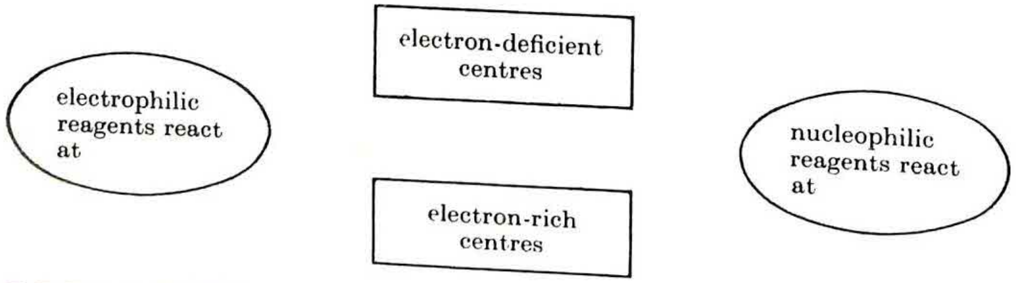
$$CH_3\cdot\overset{\overset{O}{\|}}{\underset{\underset{OEt}{|}}{C}} + \bar{C}H_2\cdot CO_2Et \rightleftharpoons CH_3\cdot\overset{\overset{O^-}{|}}{\underset{\underset{OEt}{|}}{C}}\cdot CH_2\cdot CO_2Et$$

12. (iv) Elimination of ethoxide ion to give ethyl acetoacetate which then loses a proton and remains as its anion until acidified at the end of the reaction.



$$CH_3\cdot\overset{\overset{O^-}{|}}{\underset{\underset{OEt}{|}}{C}}\cdot CH_2\cdot CO_2Et \rightleftharpoons \underset{+\ \bar{O}Et}{CH_3\cdot CO\cdot CH_2\cdot CO_2Et} \rightleftharpoons \underset{+\ EtOH}{CH_3\cdot CO\cdot\bar{C}H\cdot CO_2Et}$$

13. Bearing in mind the meaning of words such as *bibliophile* and *anglophile* join the circled words to the appropriate boxed words.


electrophilic reagents react at
electron-deficient centres
electron-rich centres
nucleophilic reagents react at

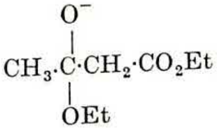
electrophilic reagents react at electron-rich centres
nucleophilic reagents react at electron-deficient centres

14. Complete the following reaction sequence by supplying the missing formula:

$$CH_3{\cdot}CO_2Et \overset{\bar{O}Et}{\rightleftharpoons} \underset{\text{(anion)}}{\text{..........}} \overset{CH_3{\cdot}CO_2Et}{\rightleftharpoons} \underset{\text{(intermediate)}}{\text{..........}}$$

$$\rightleftharpoons \underset{\text{(molecule)}}{\text{..........}} \rightleftharpoons \underset{\text{(anion)}}{\text{..........}}$$

$\bar{C}H_2{\cdot}CO_2Et$

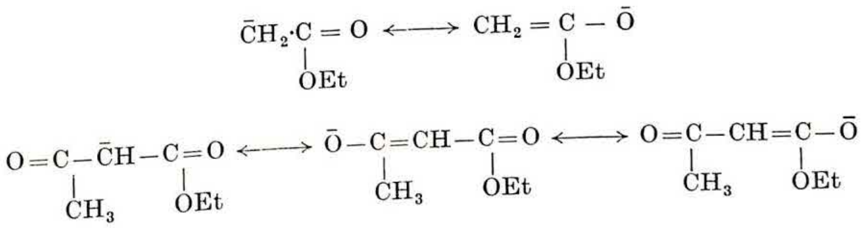


$$CH_3{\cdot}\overset{\overset{O^-}{|}}{\underset{\underset{OEt}{|}}{C}}{\cdot}CH_2{\cdot}CO_2Et$$

$CH_3CO{\cdot}CH_2{\cdot}CO_2Et$

$CH_3{\cdot}CO{\cdot}\bar{C}H{\cdot}CO_2Et$

15. Both ethyl acetate and ethyl acetoacetate can form ions by giving up protons to a basic reagent. The anions are resonance hybrids. Formulate canonical structures for the anions from ethyl acetate (two) and ethyl acetoacetate (three).



$$\bar{C}H_2{\cdot}\underset{\underset{OEt}{|}}{C}=O \longleftrightarrow CH_2=\underset{\underset{OEt}{|}}{C}-\bar{O}$$

$$O=\underset{\underset{CH_3}{|}}{C}-\bar{C}H-\underset{\underset{OEt}{|}}{C}=O \longleftrightarrow \bar{O}-\underset{\underset{CH_3}{|}}{C}=CH-\underset{\underset{OEt}{|}}{C}=O \longleftrightarrow O=\underset{\underset{CH_3}{|}}{C}-CH=\underset{\underset{OEt}{|}}{C}-\bar{O}$$

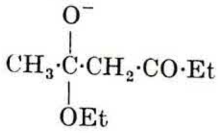
16. Ethyl acetoacetate (structure ....) is prepared by self-condensation of .... under the influence of sodium.

$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ ethyl acetate

17. Condensation requires the basic catalyst ...., produced in this reaction from .... and .... The catalyst converts the ester into its ....

ethoxide ion ($\bar{O}Et$), sodium (ethanol), ethanol (sodium), anion (or carbanion), $\bar{C}H_2{\cdot}CO_2Et$

18. This nu.................................ic reagent is a .... hybrid. The anion reacts with a second molecule of .... to form a reaction intermediate of structure ....

nucleophilic, resonance, ethyl acetate, 

$$CH_3\cdot\overset{O^-}{\underset{OEt}{C}}\cdot CH_2\cdot CO\cdot Et$$

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19. This splits out $\bar{O}Et$ to give .... which passes immediately to the anion of structure .... in the presence of the base ....

ethyl acetoacetate, $CH_3\cdot CO\cdot \bar{C}H\cdot CO_2Et$, $\bar{O}Et$

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Section 11 Source-book section Curriculum reform and work in progress

INTRODUCTION

This section contains reports on chemistry curriculum reform projects in different countries. It is hoped that they may yield fruitful ideas for others about to embark on the reform of chemistry teaching.

The CBA and CHEM Study projects have not only had a great influence on chemistry teaching in the United States, but have also catalyzed reform in many other countries. Both L. E. Strong and J. A. Campbell have recently published accounts of these projects in *Modern Chemistry and the Sixth Form* (edited by D. J. Millen), London, Collins, 1965. A critique of them from the British point of view is given in this section, and accounts of their use in countries as widely different as Italy and Japan are also included. An outline of the Nuffield Chemistry Project of the United Kingdom, which has so far produced materials for a five-year course for the 11-16 age group, and which is at present embarking on a further course for the 16-18 age group, is given. The work of OECD, starting with its seminar on the status and development of the teaching of chemistry, held at Greystones (Ireland) in 1960, and which includes publications on curriculum reform in all the sciences, has inspired chemistry curriculum reform in many countries. A selection of brief reports of such projects is given. A writing session, held at Frascati (Italy) in 1962 produced the OECD guide for teachers, *Chemistry To-day*. These reports cover only a small fraction of the countries where reform is taking place, but they have been chosen so as to be representative of as many different approaches as possible. A feature of most of these projects is the production of detailed guides for teachers and the provision of refresher courses. These are particularly noteworthy features of the revised science curricula in Ceylon and in New South Wales (Australia).

In some countries such as Switzerland and the West African countries of Ghana and Nigeria, reform has been initiated by voluntary agencies—in particular, the felt needs of the teachers themselves. In others, such as Scotland, it has come from the direct action of the Ministry of Education; in Japan university chemists have given the lead. Funds for curriculum reform have come from governmental and non-governmental sources, and from intergovernmental sources such as the Council of Europe and OECD.

Many aspects of chemistry curriculum reform remain relatively unexplored. Two major areas recommended by the OECD Working Session on the Teaching of Chemistry, held in London in 1963, for future action in planning international meetings were "The Teaching of Organic Chemistry in Schools" and "The Relationship between Physics and Chemistry in School Science". An account of recent developments in the latter area has been included. The adverse effects of many examination procedures on chemistry teaching is widely recognized as a problem in need of solution and exploratory work in the field is taking place in several countries, notably the United Kingdom and the United States. It is hoped that in successive issues of this yearbook, reports of work in these and other areas of chemistry curriculum reform will be included and that countries will send in to Unesco for inclusion reports of their own activities in curriculum reform.

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On Teaching High School Chemistry

I have thoroughly enjoyed studying these two enterprises in the teaching of chemistry at school level, and in my opinion teachers of chemistry at all levels could read these books with profit. The projects were conceived and carried through almost simultaneously in response to a widespread demand in the United States for changes in high school chemistry courses, and they had the same aim of introducing chemistry as a live, developing science. On cursory examination the routes chosen by the authors to achieve this aim are very different, but a closer look will show that very similar teaching methods have been chosen. Thus, both projects develop systematically the relations between experiment and theory, or conceptual model, and emphasize the principles underlying chemical structure, combination, and energy. They both insist that ideas should be introduced in a tentative fashion, rather than dogmatically, be examined in the light of experimental evidence, and then be accepted, modified, or discarded. Throughout each book the various principles are interwoven and developed as threads, so that they become familiar by application and use, and understood rather than learned. Each book should therefore be regarded as a systematic course, and not as an elementary reference book; in this respect, one must be cautious in sampling either book at random. Another common feature is the insistence on the value of speculative questions and discussion as a means of promoting and sustaining curiosity. Thus, in the preface to **Chemical Systems** (McGraw-Hill, New York, 1964. 772 pp., $6.96), the Chemical Bond Approach project (CBA), it is said that "Throughout the book many questions are raised. Some are raised and discussed in the text itself, while others are raised for the student to discuss. A few questions are raised to point out aspects of chemistry for which chemists do not yet have satisfactory understanding. Chemistry continues to be a development which is incomplete and in which many people participate." Similarly, in the text of the *Teachers' Guide* to **Chemistry: An Experimental Science** (Freeman, San Francisco, 1963. 480 pp., $5.80), the CHEM Study project (CS), it is said that "These questions (Questions To Wonder About) are to stimulate thinking but are not to be assigned as written work. They vary in scope and difficulty, and some have no specific answers. Discussion of some of these questions will be included soon; of others, later in the Textbook."

Now it is likely that none of these pedagogic methods is new, but they are rarely found *in extenso*, and they are woven so skillfully into the texts that the main impression, after reading these books, is of something new and refreshing. The value of the material is enhanced by the excellent production and layout of the books, with diagrams and tables that compel examination and highlight the essential information with extraordinary clarity. Teaching chemistry is revealed and sustained as a fascinating exploration, jointly conducted by teacher and pupil, and compounded of personal investigation and critical study of the work and ideas of lively minded scientists, rather than the offering of a corpus of unchangeable facts and rigid interpretations for assimilation by passive students.

In the past most school textbooks of chemistry used in Europe and America have been built around the experience of one or two teachers, albeit modified by wider discussion and criticism. The authors, with an eye to the economic barometer, have been constrained by conventional curricula and, in England, by the syllabuses of the examining boards. Far too often the result has been a careful and ponderous approach along the well-worn paths of the 19th century. Changes have been made by rearranging subject matter, or by cautious omission of some backwater and introducing hints of contemporary experiment and thinking. This is particularly true with respect to general and physical chemistry, where teaching has concentrated for too long on the tortuous emergence of the logic of the chemical evidence for the atomic theory, and on the work on gases and dilute solutions which brought fame to the great European schools of chemistry during the late 19th century. Those who find difficulty in emerging from that chrysalis of modern chemistry may be shocked on reading CBA and CS by some of the omissions that stem from the directive, "Naturally, this reconstruction of the entire course gives a unique opportunity to delete obsolete terminology and out-moded material." They will find, for example, no use of equivalent weights, only the very briefest mentions of valence (and that, in CS, to dismiss it as too confusing a noun to be useful!) and of colligative properties, and the complete absence of the law of mass action in either equilibrium or rate studies. Nevertheless, I assure such readers that in CBA and CS there is no lack of discussion of the chemical evidence for the atomic theory, for the mole concept, and for the structure of molecules; moreover, very clear pictures emerge of the factors that control chemical reaction and the transfer of matter between phases, and of the factors that lead to the establishment of chemical and phase equilibria. Some of the old, familiar (and, frankly, slightly rusty) hatpegs are missing, but the reasons why we have hats and wish to leave them in particular places are made abundantly clear.

The necessity of new approaches to the teaching of science in the United States was formally recognized some 8 years ago, when the National Science Foundation provided funds for the study and development of new courses for high schools by groups of university and high school teachers. Of the two chemistry projects chosen for support, the Chemical Bond Approach is slightly older, counting its origin from a summer school at Reed College (Portland, Oregon), in 1957. Its first texts were used in schools in 1959, and two successive revisions received wider trials in 1960 and 1961 before the final revision for the hardback editions of *Chemical Systems* and *Investigating Chemical Systems*; these appeared in 1963. The experience gained in the trials produced not only revisions of the texts but two large

Teachers' Guides. The guide to the textbook emphasizes the major ideas in the course and how they are related, develops teaching suggestions, explains suitable demonstrations, and discusses the exercises that appear in the textbook. The guide to the laboratory manual is very comprehensive; it not only advises on problems encountered in the conduct of the experiments at schools during the trial periods, and provides sample student data from these experiments, but discusses the philosophy of each experiment, the essential points that should be made in prelaboratory and postlaboratory discussions, and much supplementary information.

The Chemical Education Materials Study emerged from the work of a committee of the American Chemical Society, and was established as the CHEM Study project late in 1959. Its development followed similar lines to the CBA project, the first drafts being used in schools in 1960 and revised drafts in 1961. The final revision led in 1963 to the publication of the textbook *Chemistry: An Experimental Science* and the *Laboratory Manual*. There is a one-volume *Teachers' Guide* to the textbook and laboratory manual. In this guide the discussion of the laboratory experiments and the student exercises is slightly less thorough than in the corresponding portions of the CBA guides; but, on the other hand, the background discussions in CS appear to be somewhat deeper, and I found them more directly informative. A particularly interesting and useful feature of the CHEM Studies project is the provision of 20-minute films (16-mm sound) on a wide variety of subjects: I have found those on catalysis, ionization energy, and shapes and polarities of molecules instructive and provocative, although I have reservations about some points in others—for example, that on molecular spectroscopy overemphasises the classical concept of resonance and neglects the quantum nature of light absorption.

It would be interesting to speculate on the part played in formulating the two new approaches by the contemporary pedagogic climate, by the experimental nature of the projects through trial and revision, and by individual personalities on the teams that were responsible for the two projects. Most of the features that I have mentioned so far are common to both courses and might fairly be attributed to the first two factors. Nevertheless, with all their similarities, each project has its own distinctive flavor, and this must surely be due to more personal influences. I am not thinking of the clear differences in style, or of the innumerable small differences of presentation or example. There is a difference of depth and emphasis, which can be summed by saying that the CBA project presents a considerably more advanced and sophisticated approach, with the emphasis placed from the outset on conceptual models, and proceeds a long way with quantitative treatments of energy changes, electrode potentials, and chemical equilibrium. There is a feeling that experienced teachers are giving themselves a revision course in the fundamentals of elementary work. On the other hand, the CS project seems to be more genuinely a beginners' course, with rather more direct connection between experiment, interpretation, and theory. A good deal of thought and many difficult decisions must have been taken over the precise points at which to stop various themes in the CS textbook and transfer any further treatment into the *Teachers' Guide*. Partly because it does not attempt to go so far with some points of theory, the textbook is able to give more applications of the principles that it has introduced. Often it chooses to apply them to chemistry outside the laboratory. Thus, for example, it tells of the way that molecular structure affects the properties of proteins and of polymers; it indicates the molecular composition of living systems and applies energy cycles to metabolic processes; and it relates nuclear stability to the use of nuclear energy.

The early parts of the CBA textbook explain how to investigate and how to describe the properties of mixtures, the connections between chemical changes and heat, electrical and other forms of energy, and the electrical nature of matter. This gives a sound introduction to chemical systems and to changes in them, focusing attention on the identification of initial and final states. The text then concentrates on the space-filling property of matter, using as models first atomic nuclei or cores and electron charge clouds, next the kinetic-molecular theory, and then atomic orbitals and energy levels. The main theme of the project, which is very ably expounded, then emerges strongly to show how the nature and diversity of chemical bonds accounts for many properties of isolated molecules, of metals, of ionic solids, and of solutions of electrolytes. In these chapters, coordination numbers and oxidation numbers are fully discussed, to the exclusion of "valency," and the very thorough treatment of the mole concept seems to obviate any need for "equivalents" in stoichiometry or in dealing with ionic compounds and solutions. There are features of the electron cloud model that bother me, however. The model entails the acceptance of a large number of postulates in return for "predictions" about the shapes of polyatomic molecules. It is not at all clear why the "self-energy"—kinetic energy introduced to prevent the cloud from collapsing around the nucleus—should increase as the cloud decreases in diameter. Nor are the reasons why only two electrons can be accommodated in one cloud as attractive as the reasons for introducing the Pauli principle when relating atomic structure to the periodic table. And, when considering the gains from the postulates, it is doubtful whether the qualitative balancing of opposing tendencies would lead, for example, to the selection of N_2 and P_4 from the various possible models, if we had no experimental evidence. In many ways I wonder whether the time spent in grasping the postulates is commensurate with the gains.

In the last part of *Chemical Systems*, the CBA book, the energetics of electrical cells are used to introduce free energy, and changes in the potential of a chemical cell are linked to the distance from equilibrium of the cell reaction. In this way a realistic connection is made first between free energy changes and the tendency to move toward equilibrium, and eventually between standard free energy changes and equilibrium constants. The fundamental basis of the law of chemical equilibrium is thus provided in a convincing manner, and the equilibrium constant appears without the very dubious "proof" from the old law of mass action. The dynamic nature of chemical and phase equilibrium is suitably emphasized, however, throughout the book. Another very instructive feature of the treatment of chemical energy is the profusion of energy-level diagrams used to illustrate enthalpy and free energy changes in bond breaking, in phase changes, in the process of solution, and in chemical reactions. It is much easier for most students to grasp sign changes and algebraic differences from visual presentations than from equations. The difference between the enthalpy and the free energy of a change is identified as the organizational energy, $T\Delta S$. The resulting discussion of entropy as a measure of organization is accompanied by a wholly delightful analogy drawn from a simple ball game. Success in the game is shown to depend on the expenditure of energy and the number of targets provided at various energy levels, giving a very homely demonstration of the effects of minimizing energy demands, on the one hand, and maximizing the disorder, represented by the number of available states, on the other. This is one of the best ways I have seen of introducing a fundamental concept at an elementary level.

The strength of the CHEM Study books lies in the close relationship of experiment, principle, and theory, justifying the claim, "A clear and valid picture of the steps by which scientists proceed is carefully presented and repeatedly used." The style is personal, and there are many apt and witty comparisons between everyday behavior and the experimental method. There is repeated emphasis on careful and accurate observation, and on attention to the precision with which measurements can be made and should be reported. Atoms and molecules are brought in as working models at the start; current ideas on the structures of atoms and of molecules are introduced in chapter 6; the chemical and physical evidence for these ideas is reviewed in later chapters. In the meantime, a realistic but brief introduction has been given to chemical reactions and phase changes by linking experiments and demonstrations with discussions and exercises. I think that the CS textbook and the *Teacher's Guide* have to be considered together here; in some ways the textbook is rather lean, though the direct combination of textbook and guide might well have been too rich for the student. In this section of the book, there is a fair amount of descriptive chemistry of several groups of the periodic table, and chapters on energy effects in reactions and the factors affecting the rates of chemical reactions. The reactions chosen to demonstrate the rates in the school laboratory seem to me to be somewhat involved both chemically and mechanistically. These discussions lead to a chapter on chemical equilibrium, which contains very clear descriptions of the difference between true equilibrium and a steady state, and of the ways in which external variables affect the equilibrium proportions of the chemicals present. The equilibrium constant is introduced through direct experiments on equilibrium mixtures and generalized in the law of chemical equilibrium. This is a sound approach, not as basic as in the CBA treatment, but it is somewhat spoiled by the lack of qualification of the suggestions (in section 9.2.3 of the text and in the corresponding part of the *Teachers' Guide*) that reaction rate equations are convenient vehicles for deriving equilibrium constant expressions. This is true for single-stage reactions, but as most reactions are multistage, quite absurd equilibrium expressions can result from applying their rate laws derived under conditions far from equilibrium.

The section in the textbook on the factors that determine equilibrium is good, with another excellent analogy for "disorganization energy" in the behavior of golf balls on a split-level floor of a station wagon on smooth (low temperature) roads and on rough (high temperature) roads. This analogy is extended usefully to the effects of changing the areas available at each level, corresponding to the number of targets in the CBA scheme. However, the treatment is at a much lower pitch than in the CBA textbook. No mention is made of free energy or of entropy. In the *Teachers' Guide* some background discussion of these terms is given, but with a sad confusion of signs on page 294. The "reaction tendency" must be set equal to the *sum* of the tendency towards minimum energy and the tendency towards maximum randomness. The reaction tendency, being measured by the useful work +w which can be obtained from the reaction, must be set equal to $-\Delta F$, the tendency toward minimum energy as $-\Delta H$, and the tendency toward maximum randomness as $+T\Delta S$, giving, as required,

$$-\Delta F = -\Delta H + T\Delta S$$

or

$$\Delta F = \Delta H - T\Delta S$$

Throughout the following paragraphs the signs for ΔF and ΔH, where they represent tendencies, need similar changes, so that when ΔF is a negative quantity the reaction has a positive tendency to go.

A particularly good feature of the discussions of equilibrium in both textbook and guide is the linking of vapor pressure, solubility, partition, gas and solid dissociation, complex ion formation, and acid-base and oxidation-reduction equilibria as examples of the application of a common equilibrium law to derive the particular equilibrium constants. This procedure demonstrates the common basis for relationships that only too often are treated separately and obscured under different names (for example, dissociation constants, instability constants, dilution law, solubility product, and so on).

The middle section of the textbook deals with the physical and chemical evidence for the atomic theory, the structure and energy levels of atoms, the bonding within molecules in the gas phase, the bonding in liquids and solids, and the molecular structure of carbon compounds. These very interesting chapters include an especially clear introduction to the way in which energy levels of the hydrogen atom can be deduced from the atomic spectrum and represented by a simple expression.

The final chapters apply the principles underlying chemical structure and energy to emphasize trends in physical and chemical properties within various columns or rows of the periodic table and to explain some properties of some natural large molecules and of some living systems.

It is difficult to do full justice to these two great experiments in providing courses of instruction that take account of the fundamentals of the subject and the different needs of teacher and pupil. They have evolved courses that appear to have many good qualities in common and many good individual features, with a few aspects that might be improved. It is entirely in the spirit of the design of these experiments that, although their results may be regarded as the most useful available at the time, further modifications and fresh approaches will be needed as the subject and the objectives of the courses slowly evolve.

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Written by the staff of the Nuffield Chemistry Teaching Project for this volume.

THE NUFFIELD CHEMISTRY PROJECT

Education through Chemistry

by

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The Nuffield Chemistry Project's proposals are a contribution to the reappraisal of the place of science in education. The work outlined is intended for children of average and above average ability in the 11-16 year age group.

Most of these children will not continue to study science after the age of sixteen. For them the course must be a pertinent, satisfying and enlightening part of their school experience and must be a completed part. There are also those whose interests will take them into engineering, industry or further academic study. For this important minority, the course must also act as an adequate basis and stimulation for future work, whatever its nature. In developing the proposals, the varying needs of both groups have been kept in mind.

The bases of the proposals.

1. Pupils should have a lasting understanding of what it means to approach a problem scientifically and should have a sympathetic, yet critical, awareness of what scientists are doing and can do - this has little in common with the short-lived remembering of given information. Pupils should see science both as a way of making an enquiry and as a body of information which has been obtained by other people's enquiry. Their approach must be based firmly on experiments undertaken in the spirit of investigation, and the opportunity for exploration must be planned so that pupils develop disciplined imaginative thinking and are led to an awareness of the part that science plays in modern life.

2. The ideas discussed, the materials and techniques pupils use must, of course, be adjusted to the stage of development which the pupils have reached. They must also reflect present day scientific thought and technology.

3. Examinations, whether in class tests, school or public examinations, must demand intellectual and manipulative skills, understanding and a critical and lively mind. It is assumed that all have these qualities to a greater or less extent - our intention is to provide a course which will allow them to be exercised and developed as fully as possible.

4. An educationally imaginative outlook, expertise, and a sympathetic judgment on pupils' needs and interests are found in the teaching profession. If these essential qualities are to be fostered adequately, science masters and science mistresses must not only be given freedom from the restrictions that curtail these qualities, but also given encouragement and assistance to make use of them and to develop them. Especially we hope that those who are thinking of teaching as a career will find the opportunity for individual and creative planning, and the research that is needed, a challenge that attracts them.

Classroom implications.

If we accept these proposals, where do they lead us? They are based largely on what 'being scientific' means to a scientist - the application and personal commitment that is involved, the importance of the disciplined guess as well as logical argument; the feeling of exploration and the readiness to make apparently unwarranted jumps while knowing how to check their validity. This activity of science is nothing new and, in fact, is embryonic in much of the activity of younger children; but so far there has been little opportunity for it to take its place in the science education of the age range with which we are concerned. Obviously its effect on classroom techniques will, in many cases, be revolutionary - if only because opportunities will have to be provided for profitable 'dreaming' and the testing of 'dreams' in the spirit of Kekulé. We give here a summary of the lines along which this spirit of enquiry can be developed. Three groups of people are necessarily affected - pupils, teachers and examiners.

(a) Teachers. The burden falls squarely on the teachers' shoulders. It is true that, for many, the burden is fashioned by the demands made in public examinations. If these demand the memorization of a large body of information, this has to be our own approach. If teachers want public examinations that are sympathetic to, and encourage, the above proposals they can get them: the Examination Boards have already shown themselves to be very encouraging and cooperative.

We must have much greater freedom to select the contents and to plan the approach than is customary. Our job is to see that the classroom offers pupils an opportunity for the kinds of experience we have in mind, and that, under our guidance, it is profitable and co-ordinated. If there is to be a 'new look' it will need a 'new reaction'. This need raises many problems whose solution will call, more than ever, on that personal creative art which is the essence of teaching. Here we will only indicate some of the chief points.

1. Our major concern will be to encourage pupils to be scientific about a problem. This means that they must have a mental and manipulative skill in the exploration of a situation which, while familiar to us perhaps, is new to them. In all new situations one gropes and fumbles and is likely to make mistakes. This feeling of one's way, however, is the exercise by which judgment develops. A pupil must have graded opportunities to be either right or wrong, and he must be guided and encouraged to find out which is the case. That the pupil should see the point of experimental work is of the greatest importance. He must learn that chemicals, test-tubes, thermometers, sources of heat and of electrical energy, are tools to which he should automatically but thoughtfully turn to settle a point of curiosity or of speculation. He must learn that it is proper, not wrong, to have an opinion or an idea about something he observes - but he can't begin to think he is scientific if he does not try to check whether his idea fits experimental facts.

2. If we are to develop science teaching along these lines, the appropriate organization of laboratory work for classes of thirty or more will play a very important part. Each experimental undertaking involves three EQUALLY important stages in which the pupil must take an active part:

(a) Planning how to tackle the problem,
(b) Carrying out the experimental work,
(c) Discussing what deductions can, and - often just as important - cannot, be made from the results.

3. The introduction of theory - of molecules and ions, and of the writing of equations - raises a major problem in planning a chemistry course. This is discussed in the 'Handbook for Teachers'. Here we only want to say that speculation about material changes in terms

of molecules, ions and atoms, is the very essence of chemistry and the proposals introduce it early. From the pupils' point of view, the topic is full of the danger of unscientific, dogmatic assertions: no model should be more sophisticated than is necessary to deal with the needs thrown up by the pupils' experience. In whatever way this problem is eventually solved, we want pupils to learn to distinguish between phenomena observed and explanations put forward by the creative thinking of the human mind. From the beginning, they must be encouraged to think imaginatively about the problems confronting them, and to suggest further experiments and explanations. When they are young, many children will do this without prompting and we want this tendency to grow in precision and not to be stifled because children are afraid of being 'wrong'.

4. What should be done about the content of a course? Any present day consideration of this runs into the danger of excessive loading and this has become very serious, especially for our more able children. We, however, see this problem as arising from an attitude that regards a school subject as a corpus of information which pupils should be able to repeat - as a result, any addition is regarded as something more to learn, any omission as a loss of knowledge. A school subject need not be so regarded and content, like examinations, should be the servant, not the master. If the pupils are to feel that chemistry is 'alive', they should meet with up-to-date chemical ideas. It is true that much of the chemistry in the Nuffield scheme of work is familiar but a number of substances and experimental techniques are introduced that are not customary for the age range. In particular, importance is attached to familiarity with energy changes.

(b) Pupils. There is a very considerable increase in the maturity of pupils over the five years. The first year is one of getting the feel of what being a scientist means, of meeting new and strange materials, of learning how to do a job, of enjoying the thrill of discovery, and of learning to speak the language. It is not a time for imposed memorization of information, but a time to collect experiences, to collect ideas, to collect information, to explore new territories, and to begin to keep a science diary or note book. Pupils develop a skill in doing experiments and asking questions. As they get older, this exploration becomes more deliberate: attempts at explanations in terms of atoms, ions and molecules, become normal procedure, but pupils must realize that explanations are tentative and that they must be tested and, if needs be, adjusted, or even rejected.

(c) Examiners. Whether these are external examiners in public examinations or ourselves setting class tests and school examinations, it must be remembered that any educational scheme will be made or broken according to whether or not, at times of assessment, the demands made by types of questions are sympathetic to - indeed positively encourage - the intentions behind the scheme. It is an area of educational concern to which a great deal of thought must be given in the very near future. What are examinations trying to measure? Is it worth measuring? Is there evidence that what is done does measure it?

The form and content of the syllabus.

Present chemistry syllabuses, whatever may have been the original intention of their compilers, are predominantly lists of specific materials and of concepts. We replace these by a syllabus emphasizing manipulative and intellectual skills, and state our requirements rather in terms of prowess that should be shown than in terms of items of information that should be remembered. However, the chemistry through which pupils attain this manipulative and intellectual nimbleness and understanding, and through which they acquire the habit of demanding and assessing evidence for statements, will often be that used in older syllabuses.

A. Chemistry as a way of conducting an enquiry.

As a result of investigations and problems undertaken during the course, pupils should have acquired skill in, and understanding of, the following:-

(1) Getting new materials from those available

Bringing changes about: use of thermal and electrical energy and energy from electromagnetic radiation; adjusting the conditions of the experiment (temperature, pressure, concentration); the effects of adjustments on how fast the reaction takes place and how far it goes.

Knowing whether or not something new has been obtained - using such separation techniques as fractional and steam distillation, crystallization from water and other solvents, centrifuging, chromatography.

Using a melting point or a boiling point to test the purity of the product and using simple chemical means of finding out in what way the new products are different.

(2) Looking for a pattern in the behaviour of substances

Representing and interpreting qualitative and quantitative results, and assessing the evidence for the interpretations. Familiarity with major patterns of behaviour - examples of this are acidity and alkalinity in aqueous solutions; metallic and non-metallic nature; electrical differentiation into electrolytes and non-electrolytes; colloidal and non-colloidal systems; the periodicity of properties of elements and the conservation of mass and energy. Realizing that the importance which is placed on a pattern changes in the course of time - for example, Lavoisier's, Davy's, Arrhenius's, and Lowry and Brønsted's way of thinking about acids. Recognition of continuous gradation of properties in all classifications should arise from discussion.

(3) Using explanatory concepts and knowing how to check theory by observation.

Using the ideas of atoms, ions, molecules, giant structures and types of bonding, to explain experimental observations; planning experiments to test theoretical explanations; use of the g-atom and g-formula as an aid in this testing; the beginnings of deliberate molecular engineering in terms of chains, rings, sheets, and three-dimensional structures.

(4) Associating energy changes with material changes

Measuring the 'heat' of a reaction in simple ways; using tables of ΔHf; using energy changes in a simple way to check theory against fact by associating them with changes in energy due to bond making and bond breaking and with energies of vibration, rotation, and translation of ions and molecules.

Measuring the 'work' of a reaction and using tables of ΔGf; knowing that 'the heat' and 'the work' of a reaction have not necessarily the same value.

During the course simple investigations should be undertaken of material changes brought about by absorption or emission of U-V, visible, and I-R 'light'; e.g. photosynthesis, photography and flame-tests.

B. Chemistry as the result of enquiry.

Pupils should be aware of the work of other people. This does not mean a course of potted biography, but the opportunity to meet a few chosen examples of exciting minds and of the 'flash of genius'. Chemistry should be recognized as a product of people's activity, and the subject seen in a human perspective. For example, pupils should have some awareness of the way that the concept of an element, the concept of atoms, and the concept of energy, have developed.

An appreciation, through a few specific examples, of the way the knowledge acquired by chemists is used for meeting and fostering some of the material requirements of a community should be a deliberate intention of the course. The overall picture is either that chemical changes in raw materials can be used to supply energy for heating (ΔH) or moving (ΔG) or that energy can be used to obtain new products from raw materials.

Within this framework, considerable choice is left to the teacher to adjust the course to the interests and abilities of the pupils.

Lastly, at the end of the course, exploring the behaviour of substances should be linked with other scientific studies so that science is seen in relation to the life of the community as a whole - not only in the sense of direct application but also as an addition to a body of experience which greatly affects our lives and our sense of values.

Compiled by the staff of the Division of Science Teaching, Unesco, for this volume.

THE UNESCO PILOT PROJECT FOR CHEMISTRY TEACHING IN ASIA

1. BACKGROUND TO THE PILOT PROJECT

The newly-developing nations of Asia are quite aware that their development rests heavily upon their ability to train large numbers of their people to serve as technicians, technologists and scientists. They also are aware that they must spread an understanding of science widely among all their people to form a base for a modern industrial society. Yet their chief instruments for accomplishing these tasks - schools, technical institutes and universities - are seriously weakened by a great shortage of trained science teachers, by a scarcity of modern textbooks, and by inadequate school laboratories and apparatus. They struggle against rigid examination systems and out-dated curricula in their efforts to teach modern science. Far-reaching reform of science teaching is clearly a matter of high priority facing them.

Unesco has not been unresponsive to requests from Asian leaders for help in carrying out this reform. Through Unesco assistance, science instrument repair centres have been built; inexpensive science teaching apparatus has been supplied to schools; advisers on science curriculum reform have been sent to Ministries of Education; teacher-training institutions have been provided expert personnel, fellowships and equipment to increase their ability to prepare science teachers; and Advanced Centres for scientific work have been supplied with scientists of the highest calibre. To coordinate and intensify this assistance, Unesco has established two regional Science Co-operation Offices, one in New Delhi, one in Bangkok.

While continuing these important programmes, Unesco has recognized an urgent need for a new type of assistance to science teaching improvement. In each country in Asia, Unesco finds a small but growing corps of key science educators which is taking on more and more of the responsibility for improving science teaching. These key individuals are writing the new science textbooks needed in the schools; they are organizing and conducting in-service courses for school science teachers; they are modernizing science curricula and syllabuses and overhauling the old examination systems; and they are introducing new techniques of instruction into the schools and universities. These individuals - "the teachers of teachers" - can be found in the science departments of universities and of teacher training colleges and in the science education sections of the ministry of education. But wherever they are working, they are shouldering tasks of enormous magnitude without sufficient assistance to insure the best results of their efforts.

Consequently, Unesco's new type of programme has been focussed upon these key teachers. The strategy is to invest in strengthening their abilities as leaders of science education and to depend upon them to reflect this contribution in improvements to all those science teaching activities for which they are responsible. Besides realizing a large multiplying effect in the funds invested (an important consideration in view of Unesco's limited resources), this strategy appears sound in recognising and reinforcing initiative already present among many Asian teachers.

In planning this new programme, Unesco has been guided by several convictions regarding science teaching reform:

(a) The rapid growth of new knowledge in science makes it necessary to carry out the improvement of science teaching as a continuous process;

(b) A vital ingredient in any programme for science teaching improvement must be a dialogue between research scientists and science teachers directed toward clarifying the underlying concepts in each field of science;

(c) Science teachers must be willing to explore the usefulness of the newer techniques for instruction which are being developed by educational research.

2. OBJECTIVES OF THE PILOT PROJECT

The Pilot Project for Chemistry Teaching in Asia, the programme Unesco has established to implement this strategy for science teaching reform, is only a first step, of course, for it is limited for the moment to teachers of chemistry. Nevertheless, it is expected to provide valuable guidelines for future programmes of larger scope involving other sciences and other subjects. The Pilot Project aims to assist the key teachers of chemistry in Asia along two principal lines:

(a) Involving a selected group of them in the creative work of developing new chemistry teaching material at an experimental centre in Asia; this can strengthen their background work in modern chemistry and in the new approaches to teaching and can demonstrate to them how modern chemistry, new teaching techniques, and an integrated set of teaching materials combine to make classroom teaching more effective;

(b) Supplying carefully designed chemistry teaching materials to teachers throughout Asia as resources for the national or local level tasks they are undertaking: writing textbooks for teachers, drafting new syllabuses and examinations, conducting in-service courses for other teachers; etc. These resource materials, based upon recent content in chemistry and upon new techniques of instruction should provide a powerful stimulus to all who are preparing student materials for use in schools and universities.

This programme has been set up as a pilot programme because of the magnitude of the problems to be solved and the vast number of teachers and schools to be assisted in Asia. Only in a pilot project is it likely that reasonably manageable conditions can be assured for conducting the search for solutions to these problems, and only in a pilot project is it likely that ways can be devised to disseminate these solutions effectively to each participating country.

Furthermore, the pilot nature of the project is important in another way: it permits a demonstration to be carried out of the feasibility of involving university and research scientists in the rethinking of school-level science content. All too commonly it is assumed by school authorities and university or research scientists that school science teaching has nothing to gain from university or research scientists. Yet the lessons learned in the recent science curriculum reform projects of Europe and North America point clearly to a different conclusion: high level scientists, if involved in an appropriate manner in school science reform can make an important contribution to fundamental reform of the content of school science. The challenge facing any project that seeks to be effective is to discover those arrangements by which leading scientists may be usefully involved in reform of school science teaching. The Pilot Project has made a careful attempt to provide just such arrangements in its experimental centre in Asia and Unesco hopes the demonstration proves so convincing that the barriers preventing sincere searches at the national level for cooperation between school authorities and scientists in Asia can be overcome. This cooperation could lead to striking advances in school science reform projects in countries of Asia where scientists of world-reputation are literally waiting to find a way to be useful to their own schools and talented youth. Hopefully, the pilot project will show a way to energize these resources for science teaching improvement while keeping the guidance of schools in the hands of seasoned teachers.

3. THE PLAN OF ORGANIZATION OF THE PILOT PROJECT:

In arriving at the most effective plan for the Pilot Project Unesco has been strongly influenced by the presence in Asia of already existing national projects for science teaching reform + - many with major support from the aid programmes of the higly industrialized nations.

By locating the Pilot Project in Asia, Unesco hopes, for one thing, that benefits to science teaching will arise through a wide

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+ Ceylon, Japan, India, Philippines, Australia, Korea, Taiwan.

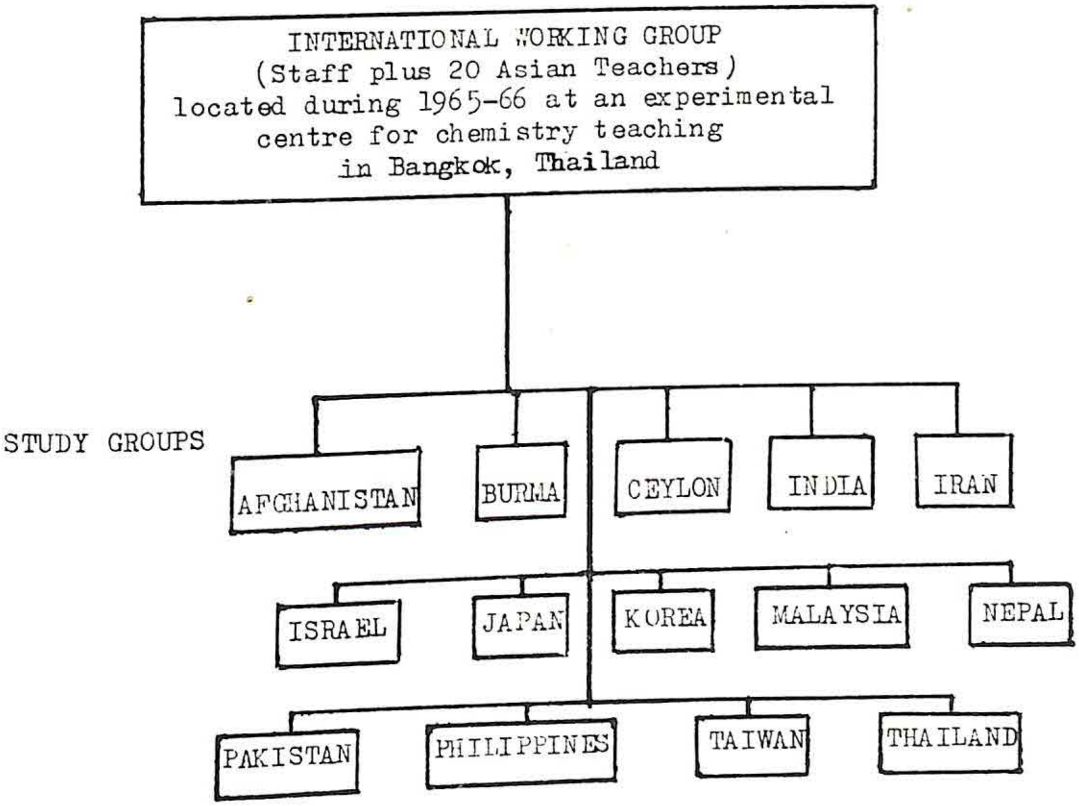
interchange of experience among leaders from these Asian curriculum reform projects who are brought together.

For another, Unesco hopes to involve these national groups in Asia who have begun science curriculum reform in the work of the experimental centre of the Pilot Project. These local groups can supply the Pilot Project a means to field test its materials during their development. In return, the Pilot Project is able to provide resource materials to the national groups for their own tasks.

The organization of the Pilot Project connects an International Working Group, located at an experimental centre for chemistry teaching with national Study Groups in each participating country of Asia. Each Study Group is supplied the resource materials prepared by the International Working Group and, after studying the materials, makes them available to individuals and groups working at the local level on various aspects of chemistry teaching reform. These groups include:

1. Chemistry teachers in universities or teacher training colleges;
2. Science education sections of a Ministry of Education;
3. Curriculum reform committees;
4. Leaders of in-service courses for chemistry teachers;
5. Textbooks-writing teams.

ORGANIZATION OF THE
UNESCO PILOT PROJECT FOR CHEMISTRY TEACHING IN ASIA


INTERNATIONAL WORKING GROUP
(Staff plus 20 Asian Teachers)
located during 1965-66 at an experimental
centre for chemistry teaching
in Bangkok, Thailand
STUDY GROUPS
AFGHANISTAN
BURMA
CEYLON
INDIA
IRAN
ISRAEL
JAPAN
KOREA
MALAYSIA
NEPAL
PAKISTAN
PHILIPPINES
TAIWAN
THAILAND

The Study Groups are supplied the resource materials in Chemistry Teaching from Bangkok and make them available to national or local units working on curriculum reform.

a. The International Working Group

During 1965-66 a group of twenty chemistry teachers from universities and teacher training institutions of fourteen Asian countries has assembled in Bangkok as the International Working Group of the Unesco Pilot Project. They are devoting a full year to study, laboratory research, and development work on chemistry teaching materials in an experimental centre for chemistry teaching. The experimental centre consists of a well equipped chemical laboratory, audio-visual materials and production facilities, offices and study rooms, and has been made available through co-operation between Unesco and the Government of Thailand. The staff and consultants for the International Working Group are being drawn from among leaders of the chemistry teaching reform projects of Asia, Europe, and the U.S.A. Other consultants include outstanding chemical research scientists and specialists in the new techniques of instruction. (+)

The International Working Group is proving useful as a channel for transfer to Asian teachers of some of the experience on curriculum reform gained in major projects outside of Asia; the Nuffield Chemistry Project in the U.K., and the CHEM Study and Chemical Bond Approach Projects in the U.S.A., for example.

Furthermore, since many of the Asian teachers in the Working Groups have taken leading parts in curriculum reform projects now underway in several of the Asian countries, the International Working Group is proving useful as a means of exchanging these experiences among the Asian teachers themselves.

Since the work at the experimental centre is organized around the preparation of resource materials in chemistry teaching, the programme at the centre includes discussions between consultants and the teachers directed toward clarifying selected topics in chemistry; individual laboratory research in a search for suitable student experiments; preparation of teaching materials based upon new techniques of learning; 8mm. film loops, programmed learning, etc.

Unesco believes that the contribution which this work in the experimental centre is making to these selected teachers is two-fold: it is providing them, as stated earlier in the aims of the project, an opportunity to strengthen their own backgrounds in modern chemistry and in an understanding of the new approaches and techniques for teaching chemistry; but it is also opening their eyes to the fact that participation in curriculum reform is now becoming widely recognized as an expected responsibility of all science teachers. It is to be thought of as normal mode of his professional life as a teacher.

b. Study Groups

Unesco has invited each participating country to organize one or more national Study Groups. A typical Study Group in a country contains university chemistry teachers, secondary school chemistry teachers, science education specialists from ministries of education, and often times a research chemist. In most cases the participation is voluntary, though in some countries a more formal arrangement has been worked out regarding membership in the Group.

The Study Groups meet at regular intervals to examine and comment critically upon the resource materials sent from the International Working Group of the Pilot Project. Unesco is also sending these Study Groups textbooks, teachers guides, laboratory manuals, films, and other teaching materials from some of the more important chemistry reform projects in the world, and as a consequence, Study Groups are able to function in each country as clearinghouses of chemistry teaching materials, a function of considerable value to teachers in schools and universities who desire access to such information.

The most important function of the Study Groups is their work in linking the International Working Group of the Pilot Project with individual or group effort in each country directed toward writing new textbooks, conducting in-service courses for chemistry teachers, or carrying on curriculum reforms. The Study Groups are bringing to the attention of these efforts the Unesco resource materials and in many cases, suggesting possible use of the materials at local levels. The Study Groups have been instructed, of course, to respect the rights of all who accept the Unesco resource materials to use them on their own terms.

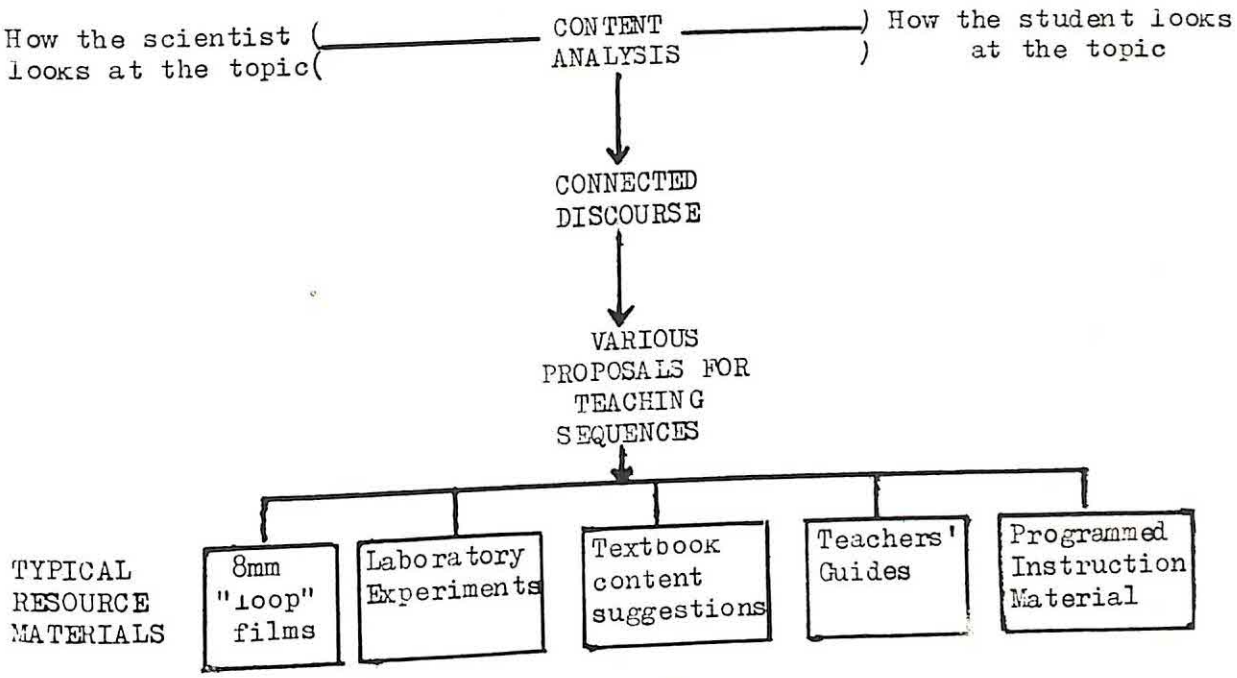
4. PREPARATION OF THE RESOURCE MATERIALS

The strategy which guides the International Working Group in preparing resource materials embraces two central propositions whose validity for science teaching reform has been suggested by work in some of the major projects mentioned earlier:

The first of those propositions raises the possibility that many attempts to improve chemistry teaching are frustrated by insufficient attention to the nature of chemistry itself. The basic question is: What could be accomplished through a careful examination by competent chemists and experienced teachers of the principles and practice that comprise chemistry? The Pilot Project asks the teachers to take this question seriously and has arranged for them to devote considerable time to a careful examination of selected areas of chemistry content. This examination, referred to as content analysis, has already indicated a variety of gaps and ambiguities in conventional presentations of chemistry.

The second of those propositions stems from preliminary experiments with new techniques of instruction. These experiments raise the possibility that a teacher's outreach and effectiveness might be considerably increased through the new techniques, e.g. 8mm film loops, programmed learning, inexpensive laboratory kits, etc. Even more important, the experiments suggest that these techniques may encourage students to shoulder more of the responsibility for their own learning of science. These possibilities are being examined by the Pilot Project. Sets of carefully integrated media for instruction prepared on the basis of analysis of each topic are being supplied to the Study Groups in each country in the hope that they will stimulate further work along the lines opened up by the International Working Group. Only a limited amount of testing of these materials with Asian school children can be attempted in the Project. Extensive adaptation and testing in actual school situations must be assumed by local groups under supervision of experts in science education

A diagrammatic presentation of the procedures followed by the International Working Group


How the scientist looks at the topic
CONTENT ANALYSIS
How the student looks at the topic
CONNECTED DISCOURSE
VARIOUS PROPOSALS FOR TEACHING SEQUENCES
TYPICAL RESOURCE MATERIALS
8mm "loop" films
Laboratory Experiments
Textbook content suggestions
Teachers' Guides
Programmed Instruction Material

A. Content Analysis

During 1965-66, three topics recognized as connecting threads in much of the chemistry taught in schools have been selected for work in the Centre by a panel of scientific advisors to the Pilot Project: (+)

Mass relationships among reacting substances;
Energy in chemical reactions;
The rôle of structure in chemistry.

(+) Report of Moscow Planning Meeting of Unesco Pilot Project, September 1964.

The analysis of each of these topics begins with questioning the adequacy of definitions of terms commonly used in textbooks. A search for "operational" ways to relate these terms with student experience leads the participants to a considerable amount of laboratory research on suitable experiments for student use. Finally, an effort is made to link each topic to other parts of chemistry. A fuller account of those procedures, as well as suggestions of additional topics likely to occupy the participants in such a Centre in subsequent years, appear in a paper by the Project Director, entitled: Content Analysis as a Major Strategy for Curriculum Reform.

The crucially important feature of successful content analysis is that the particular chemical topic under examination must be kept subject to two points of view:

1. The point of view of the scientist who insists upon reliability of evidence, experimental support of ideas, and a contemporary understanding of the topic;

2. The point of view of the student in the classroom who is attempting to understand the topic as a part of the subject of chemistry he is studying.

A balance between these two points of view is essential to any successful reformulation of a topic in chemistry. The Pilot Project participants are devoting considerable effort to attaining this balance by finding ways to overcome the usual barriers to effective dialogue between those who look on chemistry primarily as scientists and those who are concerned primarily with the way a student understands chemistry. There is little doubt that one of the most important recommendations for curriculum reform arising from this Pilot Project is that this dialogue between teachers and scientists should go on continuously within an appropriate centre to provide a constant supply of fresh thinking on what is taught in the science courses in the schools.

B. Connected Discourse

The content analysis of each topic in chemistry is finally summarized in the form of a connected discourse, often in the form of a monograph. The question then arises, "What is the best way to distribute this content over the teaching techniques available - films, texts, programmed learning material, laboratory experiments, etc." The present view in the Project is that no really reliable theory exists with which to answer this question. Instead, the experience of individual members of the project is suggesting different empirical approaches which will be compared eventually in terms of their effectiveness in aiding student understanding. This step is referred to as the preparation of teaching sequences.

C. Preparation of resource materials

One of the best ways to assist the teachers in the Pilot Project to become acquainted with modern principles of learning theory and with new techniques of instruction is to ask them to develop carefully integrated sets of teaching materials based upon these principles and techniques. Unesco has brought to the centre highly experienced consultants on such topics as audio-visual techniques and programmed instruction. The resource materials produced are to be labelled as "experimental and tentative" because more exhaustive testing of these sets under conditions of actual schoolroom use will be required to determine their validity in schools. Since in almost all countries the testing of experimental teaching materials with children in school is a prerogative of education ministries and teacher training colleges, the Unesco policy is to restrict the Pilot Project work to preparation of these sets of materials as resources for local experimentation.

D. The Search for meaningful laboratory experiments

The chemical laboratory is a central feature of the experimental centre. The Pilot Project staff and participants are devoting considerable effort to laboratory work in which a search is underway for meaningful experiments for students. The criteria for such student laboratory experiments are stringent ones:

1. The experiment should have a clear scientific purpose. While exercises to teach the use of equipment, and to demonstrate difficult principles are occasionally useful, a better experiment will provide data that answers a specific question. The best experiment provides data that answers a question at the same time that it raises new questions. In all cases, the purpose of the search must be clearly understood by the student so that the data-gathering techniques appear relevant to him.

2. The experimental techniques and apparatus must be appropriate. If the laboratory is a place for gathering ideas, then complicated equipment and difficult techniques can only get in the way. The very real problem of lack of equipment in Asian schools confronts the Pilot Project with the task of searching for simple procedures using the most readily available chemicals and the most familiar types of apparatus.

3. The experiment should be honest according to the best available knowledge of the underlying chemistry. Often, by selecting specific reactions or specific conditions, one can use a false experiment to gather good data. However, the end does not justify the means. Chemical problems should be faced squarely, and the spurious experiment discarded, or else put in a context where its falseness is brought to light.

4. The experiment should be reproducible by the class of students who use it. Careless work should never be encouraged: measurements should be made to the limit of convenient accuracy, unless it is knowingly done to gain an order of magnitude estimate. Such matters as errors in measurement, significant figures and reproducibility are a necessary part of the laboratory procedure.

5. The experiment should encourage genuine independent inquiry. The pursuit of chemical fact and theory is a never-ending quest. In such experiments, even the unimaginative student can be made to see the need for and be inspired to do unscheduled but supervised work.

Compiled by the staff of the Division of Science Teaching, Unesco, for this volume.

OTHER PROJECTS FOR THE REFORM OF CHEMISTRY TEACHING

Australia

A major reform in the teaching of all the sciences has recently taken place. In New South Wales, under the auspices of the Nuclear Research Foundation, a six-year integrated science course has been designed in which the subjects astronomy, physics, chemistry, biology and geology are treated as a whole. The aim of the originators of this course is to enable the student to view science as a whole and not to look upon it as "bits". In addition, it is intended that the integrated course should provide a maximum amount of basic general knowledge for those whose only instruction in science will be this course, and maximum scope for specialisation for those who wish to go further. In order to achieve this, the text-book* for the first four years of the course has been written to cover three levels - Ordinary, Credit and Advanced.

The fundamental thinking on which the chemical aspects of the course were based was carried out at summer schools for chemistry teachers held at the University of Sydney, during 1961 and 1962. The ways in which modern developments in various aspects of chemical theory could be made the basis of school chemistry courses were explored. Working Groups considered the teaching of topics such as "Equilibrium and Chemical Reactions", "Atomic Structure and Chemical Bonding", "Oxidation, Electrolysis and Acid - Base Theory", and "Nuclear Chemistry" in terms of depth, order of treatment and general teaching approach. Recommendations were made as to what material would be appropriate at different age and ability levels of pupils. A working group on Organic Chemistry recommended that this subject should be integrated with inorganic and physical chemistry so that chemistry can be taught as a single co-ordinated subject.†

In addition to text-books for pupils, a comprehensive teachers' manual has been drawn up to assist teachers in the implementation of the new syllabus and the use of the text-books. Each chapter of this manual, gives detailed references to source material, and suggests appropriate apparatus, experiments, visual aids and models to illustrate the relevant chapter of the pupils' book, as well as outlining a recommended teaching approach. The Working Groups of university lecturers and school teachers who both drew up the syllabus and wrote the text-books to accompany it will continue to carry out amendments and adaptations to the course as the need arises, so that it is kept up-to-date.

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* Science for High School Students text-book series, world publishing rights, Pergamon Press Ltd., Oxford, U.K.

† An account of these Summer Schools is available in "Approach to Chemistry, 1961" and "Approach to Chemistry, 1962", University of New South Wales, Sydney, Australia.

Ceylon

A major project for the development and reform of science teaching in Ceylon was launched in 195 with assistance from Unesco and funds from both government and bi-lateral aid sources. New schemes of work in all the sciences have recently been introduced into the schools after extensive trials over a period of two years. The scheme was drawn up by working groups of local teachers with leadership from experts with overseas experience of curriculum reform. Schools have been provided with laboratories and equipment for the courses and also with tool-kits so that simple apparatus can be improvised, making use of local materials. Refresher courses for teachers based on the new schemes of work have been organised, and the training of science teachers is also related to the schemes.

The chemistry outline gives detailed recommendations for teaching approaches, experimental procedures and tests. The teacher is not, however, constrained to adhere rigidly to the treatment suggested, provided he gives a similar content of instruction to his pupils. In drawing up the schemes, there has been an attempt to move away from the teaching of the stereotyped preparation and properties of a number of apparently isolated chemical entities in favour of a more thorough treatment of chemical reactions. Selection of the reactions to be studied was based partly on their importance from a fun ctional aspect in a Ceylon context and partly on their effectiveness as illustrations for teaching chemical principles in Ceylon schools. The whole course is based on a foundation of practical work, much of it of an individual nature.

Czechoslovakia. (Information supplied by Professor J. Zyka, Head, Department of Analytical Chemistry, Charles University, Prague, and Dr. A. Schütz, Department of Physical Chemistry, Charles University.)

The training of secondary school chemistry teachers has received considerable attention recently in Czechoslovakia, and the system which has now been worked out has been found to be highly effective. It is an improvement on the older system in which school teachers were educated entirely in the Natural Science faculties of the universities, and also on the system which superseded it in which independent colleges of education were instituted. The latter system was found unsatisfactory because the separation of teacher training from the universities caused a decline in the quality of the education.

In the system which is now in operation, the aim is to develop good chemists as well as good teachers. Students intending to become secondary school chemistry teachers enrol at the university (the Faculty of Natural Science) for a five-year period of study. The receive training in two science subjects e.g. Chemistry-Physics or Chemistry-Biology. For the first three years, the syllabus followed by students attached to the pedagogical branch is practically the same as that of the chemistry research branch, and the same professors supervise the work in both branches. In the third year, the two branches separate and the prospective teachers include in their programmes courses in methods of chemistry teaching and educational psychology, the former being taught by chemistry lecturers who have special responsibility for pedagogical students. They also visit schools and take part in practice teaching. In their final year they prepare a diploma thesis which must deal with a specialized topic in chemistry, be original work, and present a view of a part of some field of science, discussing the application of this review to school-science teaching. Quite often the diploma theses of prospective secondary school teachers are similar to those of prospective research chemists. The final examination is in all branches of chemistry.

University chemistry staff take part in all activities connected with secondary school chemistry teaching. Recently the Ministry of Education and Culture created a special advisory committee to review the syllabus and curriculum both of the universities and the secondary schools. A special section of the Czechoslovakia Chemical Society has been established to consider the problems of chemistry teaching. Postgraduate courses on recent developments in chemistry are being organised for teachers, lead by outstanding research experts and scientists from the universities and the Academy of Sciences; these courses include laboratory work.

Ghana and Nigeria

New chemistry syllabuses at both the School Certificate and Advanced Level have been approved by the West African Examinations Council.

The preliminary work for both these syllabuses was carried out by the Ghana Association of Science Teachers, a voluntary organisation, whose working parties set out to produce chemistry courses which were up-to-date in content and method, and also related to the West African environment. These working parties were made up of practising school teachers and university lecturers in chemistry and education. Recent work on chemistry curriculum reform from the USA, U.K. and Australia was brought to bear on the design of the new syllabuses, as was the O.E.C.D. Report of the Greystones Seminar.

In both syllabuses, considerable pruning of content has taken place, and topics were only included if they could be justified as fundamental to an understanding of the subject or as having important applications in West Africa. In the Advanced level syllabus the emphasis on basic principles is placed particularly on the concepts of structure and energy as they apply to chemical systems; and in the School Certificate syllabus, more emphasis is placed on atomic structure than has previously been the case at this level of teaching. The fundamental importance of practical work is brought out in both syllabuses.

Refresher courses for chemistry teachers have been held in both Ghana and Nigeria during the last two years. Plans are now being drawn up to produce teaching materials to accompany the new syllabuses.

Hungary

1. Modern Teaching Methods.

Dr. Pais, Professor of Chemistry in the Chemical Department of the College for Horticulture in Budapest, reports that an increasing number of chemistry teachers in Hungarian high schools is studying the simpler aspects of 'programmed learning', although he does not think that the method will ever have a predominant place in chemistry instruction in Hungary. On the other hand, chemistry instruction by television, begun only a year and a half ago, has already become significantly important. So far, two programme series have been initiated - (1) a series of 18 lectures, covering the secondary school first year curriculum, for adult students (evening classes and correspondence courses): (2) a programme broadcast once a month to assist chemistry teaching in grade 7 (age 13) of the elementary schools. These broadcasts are not intended to be a substitute for the teacher, but they make possible demonstration experiments which are beyond the resources of an average school. Films are presented to set the mood for the discussion of a given topic, and to demonstrate the practical application of the element or compound. Students are thus encouraged to see the relation between what they study and everyday life, and they acquire knowledge which could otherwise only be obtained by time-consuming visits to factories. Cartoons have been extremely successful in demonstrating chemical principles such as reversible processes and chemical equilibrium, Avogadro's Law etc. Closed-looped television has also been used successfully in training chemistry teachers. Well-trained teachers give lectures in model schools, organized by the universities. These lectures are transmitted by built-in cameras and microphone into a lecture hall where 30-40 would-be teachers can observe the lesson without disturbing it.

2. Curriculum changes - work in progress.

Dr. K. Garami, Department of Chemistry, National Pedagogical Institute, Budapest, reports on curriculum reform since 1962. Chemistry teaching begins in the 7th form and continues in the 8th form of the general (elementary) schools (ages 10-14), and then in the grammar schools. Efforts are being made to introduce atomic structure at an early stage so that it can be used as a basis for arranging the material covered by the course.

Current research work on the grammar school curriculum features the introduction of wave-mechanics, bonding, energetics, structure and mechanism in organic chemistry. Dr. Garami expresses the view that programmed instruction may play an important part in the modernization of chemistry teaching.

Italy (Information supplied by Professor A. Liberti, Institute of Analytical Chemistry, University of Naples.)

Activities for the improvement of the teaching of chemistry in secondary schools were based on the recommendations of the O.E.C.D. Greystones Seminar on chemistry teaching (1960). A national committee for chemical education has been established whose membership includes university professors, Ministry of Education officials and secondary school teachers. The Committee has supervised a pilot project* in chemistry teaching and is evaluating its results. The pilot project is partially based on CHEM Study material and its stages of implementation have been as follows:-

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* sponsored by O.E.C.D.

(i) A seminar for 70 school teachers was held in Rome in the Spring of 1963, and 25 of these teachers were selected for participation in the pilot experiment.

(ii) A training course of three weeks was held in the summer of 1963 for the 25 teachers.

(iii) The 25 teachers directed in 1964-65 pilot classes in schools of different types, according to a new syllabus, and followed a text-book "Lezioni di Chimica" and a manual of experiments drawn up by the national committee.

(iv) In 1965 the experiment was doubled and 80 pilot classes have been in operation. There will be a further extension in 1966.

The teachers involved in the pilot project have been relieved of some of their teaching assignments to give them more time for the organisation of the work and preparation of the experiments; also the working time for the students was increased by about one hour per week to make time for the laboratory work. Schools with pilot classes were equipped with up-to-date chemistry laboratories, as previously students were learning chemistry without carrying out experimental work. The text-book "Lezioni di Chimica" and the manual of experiments which emphasise the experimental approach to the teaching of chemistry are intended to serve as a pattern and as a reference book for text-book writers and for teachers who wish to keep up with new methods of teaching.

The results of the project have been very encouraging. The pupils enjoy the experimental approach to learning chemistry and have reached a high standard in their work. There has been a general improvement of text-books available on the market and the elimination of the more common errors. The impact of the pilot class experiments on the teaching of chemistry in the secondary schools over a period of two years has been quite remarkable, and soon its effect will be felt also at a higher educational level.

Japan

(Information supplied by Professor M. Oki, Department of Chemistry, the University of Tokyo.)

The Chemical Society of Japan established in 1952 the Committee of Chemical Education which has been actively engaged in the modernisation of chemical education. A series of lectures on the C.B.A. projects given in 1961 by Professor A.H. Livermore lead to three summer institutes in 1962 at which this project was discussed in detail; two lecturers were invited from the USA and there was 120 participants. In 1963-64, lectures given by Dr. J.A. Campbell lead to a request for a series of institutes on the Chem. Study Project in 1965. Plans are now being drawn up for a revision of the teaching of chemistry for the 15-18 age group, and it is intended to draw up a prototype text-book. Centres for the re-training of teachers are already actively in operation and will be used to familiarise teachers with the new materials. The Committee of Chemical Education has also made a general survey of the teaching of chemistry at college level as a preparation for reform. In November 1964, a group of chemistry professors from the USA and Japan met to discuss college chemistry curricula. As a result of this meeting it was agreed that information should be exchanged on the re-organisation of chemistry curricula and the relation between college and high school chemistry.

Switzerland (Abstracted from school chemistry reform in Switzerland by Dr. C. Kauter, School Chemistry, O.E.C.D.)

As there are no government grants to assist in curriculum revision, it is left to private initiative to reform the methods of teaching chemistry. The Swiss Society of Science Teachers has a special section and committee to deal with all matters concerning chemical education. This committee organised voluntary courses to bring the ideas of the Greystones Seminar of O.E.C.D. into perspective with Swiss Education. The Swiss Chemical Industries financed these courses. In March 1963, the new syllabuses were introduced involving new concepts in the teaching of chemistry. Two text-books have been prepared to accompany these courses, drawing on material from CHEM Study and C.B.A.

United Kingdom

Scotland (From Present Trends in the Teaching of Chemistry, by D.G. Chisman, School Chemistry, O.E.C.D.)

New syllabuses for the Scottish Certificate of Education in physics and chemistry were introduced in 1962 and were offered as alternatives to the more traditional type of syllabus. About two-thirds of the schools have adopted the new syllabus. In chemistry, the concepts of energetics, chemical bonding and atomic structure have been borne in mind throughout in an attempt to make the approach more logical than in the past. In addition, many modern topics have been introduced and out-dated ones omitted in order to make the early part of the work of value to the ordinary citizen.

The teachers have responded enthusiastically. Refresher courses for teachers have been held and memoranda on specific topics are available (ref. circular 512, Scottish Education Department, to be purchased from H.M. Stationery Office, 13A, Castle St., Edinburgh 2).

Compiled by the staff of the Division of Science Teaching, Unesco, for this volume.

THE RELATIONSHIP BETWEEN PHYSICS AND CHEMISTRY IN PRE-UNIVERSITY AND FIRST-YEAR COLLEGE SCIENCE COURSES.

A closer integration between physics and chemistry teaching in schools as a preparation for university work or in first-year university classes is being sought in several parts of the world, notably Great Britain and USA. A Physical Science Committee recently set up by the Association for Science Education of Great Britain has produced an interim report "Physical Science as a Sixth Form Subject".* The report suggests that in order to rationalize and broaden in scope the pre-university science curriculum a new subject "Physical Science" be devised. This would provide an opportunity for building up a course with a recognisable shape of its own in which the "physical" and "chemical" approaches would complement one another. A possible shape would involve a progression from fundamental ideas of force, energy and electricity to a consideration of macroscopic and physical systems. The fundamental ideas might well include periodic motion and wave motion, a consideration of fields, and some work on A.C. theory and simple electronics. These basic concepts would be applied, not only in conventional situations, but also to atoms and molecules. Such a course could be used to show how the methods and principles of scientific investigation are used, and it could give opportunities for mathematical formulation and development of theories side-by-side with laboratory work. The course would have to be flexible and might include a common core of basic material and a number of options. It would give ample opportunity for the discussion of technological and other applications and would also allow scope for "project" work.

Various college and universities in USA† have instituted joint Physics/Chemistry courses for their first year students. In an article, "Combining first year college chemistry and physics for students majoring in science[†]", Dr. Edward C. Fuller, of Beloit College indicates that colleges which have instituted these courses have found advantages in them of both an educational and a practical nature. From an educational point of view, the integrated course can help students to understand the fundamental dependence of modern chemistry on physics, and students can also come to a deeper understanding of fundamental concepts such as kinetic-molecular theory by applying them to both chemical and physical systems. Practical advantages are numerous. Exposing students to both physics and chemistry in their first year of college enables them to make a much better choice of major, and by eliminating overlap between physics and chemistry there can be a considerable saving of time. The combined course is especially valuable in the curriculum for preparing students to become secondary school science teachers, since they are often expected to teach both sciences.

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* "Association for Science Education Bulletin", September 1965, pp.16-32.

† These include Beloit College, Carleton College, Cornell College (Iowa), Lawrence College, Reed College, the University of Southern Florida, Wabash College and Whitworth College.

The courses vary from one institution to another, but commonly they are centred round studies of the structure of matter and its interactions with energy in the form of heat, electricity and electromagnetic radiation. Coherence may be given to the course through syntheses of ideas such as "Elements and Chemical Change" (composition, structure and energy), "Fields" (gravitational, electric, magnetic and nuclear) and "Thermodynamics" (statistical mechanics, heat, and kinetic theory). In some courses, the selection of a broad theme to be threaded through the course helps to focus students' attention on the scientific process. Such themes include "Developing a Model of the Universe","Transformations of Matter and Energy" and "Particles and Atomicity".

The running of these courses creates administrative problems at times and there may also be difficulties in finding suitable text-books. The staff of almost all of the colleges offering an integrated course have prepared their own laboratory manuals. Those who have taught integrated courses feel that these disadvantages are outweighed by the advantages of integration, and none of them plan to return to separate introductory courses.

[†] "Experimental Curricula" in Chemistry, Report of the Advisory Council on College Chemistry Conference 1963, pp. 19-28.

Some other plans for joint Physics/Chemistry courses include the following:-

1. A group in Portland, Oregon, USA, is at present studying the integration of PSCC Physics and CBA Chemistry into a combined two-year course. A group in U.K. is doing the same for PSSC and CHEM Study Chemistry.

2. Various universities and technical colleges in the U.K. e.g. the universities of Sussex, Reading and Oxford, and Woolwich Polytechnic have instituted combined Physics/Chemistry courses or courses in "Materials Science".

3. The integrated science course devised in New South Wales, Australi has achieved a much closer integration between physics and chemistry teaching than hitherto.

JOURNALS AND PERIODICALS OF RELEVANCE TO CHEMISTRY TEACHERS

The following list of journals and periodicals includes both chemistry journals and publications of a more general educational and scientific nature which contain articles relevant to chemistry teaching. This is only a preliminary listing and information on other journals which chemistry teachers find valuable would be welcomed.

ARGENTINA

Anales de la Asociación Química Argentina. Asociación Química Argentina, Hipólito Yrigoyen 679, Buenos Aires.

AUSTRALIA

Australian journal of chemistry. Commonwealth Scientific and Industrial Research Organization, 314 Albert Street, East Melbourne C.2.

The Australian science teachers' journal. The Australian Science Teachers Association, Sydney Teachers' College, Newtown, New South Wales.

AUSTRIA

Mitteilungen des Vereins zur Förderung des Physikalischen und Chemischen Unterrichts, Schelleingasse 39/10, Wien IV.

BELGIUM

Bulletin, Sociétés Chimiques Belges, 39 rue des Moutons, Louvain.

BRAZIL

Anais da Associação Brasileira de Química. Associação Brasileira de Química, Caixa Postal 550, Rio de Janeiro.

BULGARIA

Biologija i Himija. Ministerstvo na prosvetata i Kulturata, Ul. W. Drumev 37, Sofia.

CANADA

Canadian journal of chemistry. National Research Council, National Research Council, Ottawa 2.

CHILE

Boletín de la Sociedad Chilena de Química. Sociedad Chilena de Química, Casilla 169, Concepción.

FRANCE

Bulletin de l'Union des Physiciens. L'Union des Physiciens, 44 Bd. Saint-Michel, Paris-6e.

GHANA

Ghana Association of Science Teachers bulletin. Ghana Association of Science Teachers, University College of Science Education, Cape Coast.

HUNGARY

A Kémia Tanitása. Müvelödésügyi Minisztérium, Szalay utca 10-14, Budapest V.

INDIA

Vigyan Shikshak. All-India Science Teachers' Association, H. 2/3, Model Town, Delhi 9.

ISRAEL

Israel journal of chemistry. Weizmann Science Press of Israel, P.O. Box 801, Jerusalem.

ITALY

Chimica. Istituto Italiano di Storia della Chimica, Via Quintino Sella 2, Milan.

JAPAN

Nippon kagaku zasshi. No. 5, 1-chome, Surugadai-Kanda, Chiyoda-ku, Tokyo.

Rika no kyôiku. Tôyôkan Shuppan-sha, 2-13 Kanda Awaji-chô, Chiyoda-ku, Tokyo.

MEXICO

Boletín del Instituto de Química. Universidad Autónoma de México, Mexico D.F.

NEW ZEALAND

New Zealand school science. Westlake High School, Auckland, N.2.

PERU

Boletín de la Sociedad Química del Perú. Casilla 891, Lima.

PHILIPPINES

Science bulletin. Science Foundation of the Philippines, 1580 Taft Avenue, Corner Herran, Manila.

POLAND

Przemysl chemiczny. Zuravia 6/12, Warszawa.

Chemia w szkole. Plac Dabrowskiego 8, Warszawa.

ROMANIA

Revue Roumaine de chimie. Academiei R.P.R., Str. Gutenburg 3 bis, Bucureşti.

Ştiinţa si tehnica. Comitetul Central al Uniunii Teneretubui Muncitor şi Societatia pentru Raspindirea Stiinţei si Culturii, Piaţa Scinteii 1, Bucureşti.

SPAIN

Real Sociedad Española de Física y Química. Anales serie B : Química. Facultad de Ciencias, Ciudad Universitaria, Madrid 3.

SWEDEN

Svensk kemisk tidskrift. Farlag Svenska Kemist samfundet, Stockholm.

SWITZERLAND

Chimia. H. R. Sauerlander & Co., Larwenzenworstadt 89, Aarau.

TANZANIA

START journal. Science Teachers' Association of Tanzania, St. Andrew's College, Minaki, Tanzania.

UGANDA

Science teachers' journal. The Uganda Science Teachers' Association, P.O. Box 262, Kampala.

UNION OF SOVIET SOCIALIST REPUBLICS

Himija v Škole. Metodičeskij Žurnal. Ministerstvo Prosveščenija R.S.F.S.R., 3 proezd Mar'inoj Rošči, 41, Moskva.

UNITED ARAB REPUBLIC

Majallat al-ʿUlūm al-Hadīthah. Rābiṭat Mudarrisī al-ʿUlūm bil-Jumhūriyah al-ʿArabiyah al Muttaḥida, Taftīsh al-ʿUlum, Mabna al-Mujamma, Maydān al-Taḥrīr, Cairo.

UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND

The school science review. Association for Science Education, 52 Bateman Street, Cambridge.

Education in chemistry. Royal Institute of Chemistry, 30 Russell Square, London, W.C.1.

The science teacher. Junior Club Publications Ltd., 60 Paddington Street, London, W.1.

UNITED STATES OF AMERICA

Journal of chemical education. Division of Chemical Education of the American Chemical Society, College of Wooster, Wooster, Ohio.

Chemistry. American Chemical Society, Earlham College, Richmond, Indiana.

Chemical and engineering news. American Chemical Society, 1155 Sixteenth Street N.W., Washington, D.C. 20036.

VENEZUELA

Revista de la Sociedad Venezolana de Química. Sociedad Venezolana de Química, Apartado 3895, Caracas.

S.C.E.R.T., West Bengal
Library
Calcutta
25/3, B. C. Road

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